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## FACSIMILE COVER SHEET

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DATE: November 3, 2008

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Group Art Unit 1754

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612.746.3006 faxApplication No.: 09/757,519  
Applicant: Home et al.  
Due Date: November 16, 2008

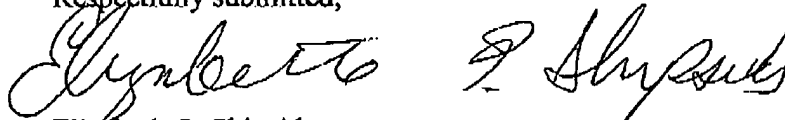
OUR REF.: 3132.07US02

FROM: Elizabeth Q. Shippides  
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Attached is the following for filing in the above-identified application.

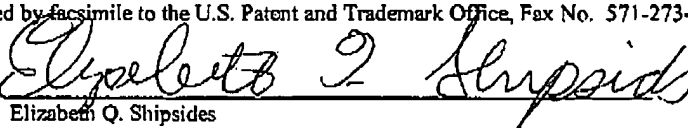
- (1) Appeal Brief Transmittal (1 page);
- (2) Appeal Brief (26 pages);
- (3) Claims Appendix (4 pages);
- (4) Evidence Appendix with Three Patents (24 pages); and
- (5) Related Proceedings Appendix with Decision (8 pages).

Respectfully submitted,

Elizabeth Q. Shippides  
Registration No. 57,529

## CERTIFICATE OF FACSIMILE TRANSMISSION

I hereby certify that this paper is being transmitted by facsimile to the U.S. Patent and Trademark Office, Fax No. 571-273-8300 on the date shown below.

November 3, 2008  
Date  
Elizabeth Q. Shippides

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NOV 03 2008

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Attorney Docket No.: 3132.07US02

Home et al.

Confirmation No.: 8679

Application No.: 09/757,519

Examiner: Edward M. Johnson

Filed: January 9, 2001

Group Art Unit: 1754

For: METAL VANADIUM OXIDE PARTICLES

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BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

BRIEF FOR APPELLANT

NOV 03 2008

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Attorney Docket No. 3132.07US02

## APPEAL BRIEF TRANSMITTAL

In re the application of:

Horne et al.

Confirmation No.: 3132.07US02

Application No.: 09/757,519

Examiner: Johnson, Edward M.

Filed: January 9, 2001

Group Art Unit: 1754

For: METAL VANADIUM OXIDE PARTICLES

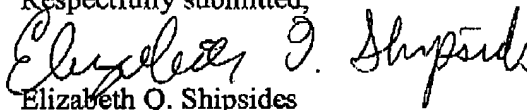
Mail Stop Appeal Brief-Patents  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

Transmitted herewith, is the Appeal Brief in the above-identified application, with respect to the Fourth Notification of Non-Complaint Appeal Brief mailed October 16, 2008.

Applicants previously paid \$250 for the filing of an Appeal Brief in this matter on August 20, 2003. Applicants believe that no additional fees are due, but please charge the below deposit account if that assessment is in error to ensure entry of this Brief.

Respectfully submitted,



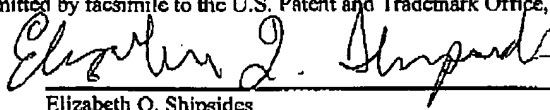
Elizabeth Q. Shippersides  
Registration No. 57,529

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November 3, 2008  
Date

  
Elizabeth Q. Shippersides

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Application No. 09/757,519

## PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Attorney Docket No.: 3132.07US02

Horne et al.

Confirmation No.: 8679

Application No.: 09/757,519

Examiner: Edward M. Johnson

Filed: January 9, 2001

Group Art Unit: 1754

For: METAL VANADIUM OXIDE PARTICLES

BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES  
SECOND CORRECTED APPEAL BRIEF

Mail Stop Appeal Brief - Patents  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

INTRODUCTORY COMMENTS

This is an appeal from an Office Action dated July 16, 2007, in which claims 1-3, 10, 17-22, and 24-29 were finally rejected. The rejection of claims 1-3, 10, 17-22, and 24-29 are hereby appealed. A Notice of Appeal was filed on August 7, 2007. A fourth Notice of Non-Compliant Amendment was mailed October 16, 2008. This fourth Corrected Appeal Brief is timely filed in response to the Notice of Non-Compliant Brief of October 16, 2008. Please note that the Evidence Appendix coversheet includes a statement setting forth where in the record that the evidence was entered by the Examiner.

*Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 50-3863.*

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November 3, 2008  
Date

  
Elizabeth Q. Shippides

**REAL PARTY IN INTEREST**

Greatbatch, Ltd. (previously known as Wilson Greatbatch Technologies, Inc.), has acquired the entire right, title and interest in and to the invention, the application, and any and all patents to be obtained therefore. Greatbatch was assigned the patent application by NanoGram Corporation, a corporation organized under the laws of the state of Delaware, and having offices at 165 Topaz St., Milpitas, California. On June 17, 2004, an assignment was executed transferring ownership from NanoGram Corporation to Wilson Greatbatch Technologies, Inc. recorded at reel 015552, frame 0199, although NanoGram Corp. may have retained certain licensed rights. The rights in the patent application were transferred to NanoGram Corp. as per the Assignment, recorded at Reel 011451, Frame 0570 from the inventors to NeoPhotonics Corporation and an assignment from NeoPhotonics Corporation to NanoGram Corporation recorded at Reel 013957, Frame 0076. Note that NeoPhotonics Corporation was formerly called NanoGram Corporation, and the present NanoGram Corporation is an independent corporation spun out from NeoPhotonics Corp.

**RELATED APPEALS AND INTERFERENCES**

U.S. Patent application 09/606,884 was appealed to the USPTO Board of Patent Appeals and Interferences. This application has now issued as U.S. Patent 7,214,446. This patent is assigned to NanoGram Corporation. A copy of the decision is attached. It is noted that the decision reversed the rejection.

**STATUS OF CLAIMS**

Claims 1-3, 6-18 and 22-29 are pending. Claims 4, 5 and 19-21 have been cancelled. Claims 1-3, 10, 17, 22, and 24-29 stand rejected. **The rejection of claims 1-3, 10, 17, 22 and 24-29 is presently appealed.** Claims 6-9, 11-16, 18, and 23 are free of any rejections and are objected to for depending on a rejected base claim.

In multiple Office Actions from December 28, 2001 through January 27, 2003, Examiner indicated that claims 11-16 and 18 contained allowable subject matter. After Applicant filed a Notice of Appeal and multiple Appeal Briefs beginning on August 20, 2003, Examiner issued a non-final Office Action dated February 7, 2007 without considering pending claims 11-16 and 18. Applicant notes that the Patent Office lost an initially filed Appeal Brief and significant delay resulted. The Office Action of February 7, 2007 had an error with respect to dropping claims 11-16 and 18 from the application. Applicant inadvertently propagated this error in a Response filed on May 11, 2007. Applicant maintains that these claims were never canceled and remain pending and allowable.

The appealed claims are listed in the Claims Appendix.

#### **STATUS OF AMENDMENTS**

All Amendments have been entered with the filing of the Appeal. No after-final amendments were submitted.

#### **SUMMARY OF CLAIMED SUBJECT MATTER**

The invention relates to powders, i.e., collections of particles, having a composition of a metal vanadium oxide. (See, for example, the abstract.) Metal vanadium oxides have a non-vanadium metal ion along with a vanadium ion within an oxide composition. (Specification, for example, page 4, lines 10-23.) The claimed composite metal oxide particles have an average particle size less than a micron. (Specification, for example, page 5, lines 1-18. Figs. 11 and 12, for example.)

Any particular powder has particles that can be characterized by size. A collection of particles has an average particle size and a distribution of particle sizes, which are related but separate properties. The distribution of particle sizes relate to the size uniformity of the particles.

Some of the pending claims specify particular distributions corresponding to highly uniform particles. (Specification, for example, page 31, lines 3-26. Fig. 12, for example. Claim group 4.) All of the claims directed to particle collections have a submicron average particle size. (Specification, for example, page 30, lines 1-19. Figs. 11, 12, 15, and 16, for example. Independent claim 1. Claim group 1.) In some embodiments, the particles have an average particle size from about 5 nm to about 100 nm (claim group 2), and in further embodiments, the particles have an average particle size from about 5 nm to about 50 nm (claim group 3). (Specification, for example, page 30, lines 1-19. Figs. 11, 12, 15, and 16, for example.). In some embodiments, the metal vanadium oxide is crystalline. (Specification, for example, page 32, lines 10-14. Figs. 9-12, for example. Claim group 5).

Some of the pending claims relate to methods for forming metal vanadium oxide particles. (Independent claim 10. Claim group 4.) In the claimed methods, the metal vanadium oxide particles are formed by heating a mixture of vanadium oxide particles with a non-vanadium metal compound. (Specification, for example, page 26, line 29 to page 27, line 10. Figs. 6 and 7, for example.) The **reactant** vanadium oxide particles have an average particle size less than a micron. (Specification, for example, page 27, lines 11-22. Fig. 16, for example.) Applicants' specification describes the formation of submicron vanadium oxide particles using a process called laser pyrolysis. (Specification, for example, page 4, lines 26-33 and Example 1. Fig. 1, for example.). Through the description of the laser pyrolysis approach, Applicants' specification enables the formation of the starting materials for the formation of submicron metal vanadium oxide materials. (Specification, for example, page 5, lines 1-18 and page 6, lines 18-27. Figs. 1-6, for example.) The present application does not claim the formation of particles with laser pyrolysis.

Additional claims are directed to batteries formed with submicron metal vanadium oxide particles. (Independent claim 17. Claim group 1.) In particular, metal vanadium oxide particles are useful as cathode materials, especially for lithium-based batteries. (Specification, for example, page

34, line 14-page 36, line 24. Fig. 8, for example.) The submicron character of the metal vanadium oxide particles can contribute improved performance in battery applications. (Specification, for example, page 34, line 14-page 36, line 24. Fig. 8, for example.)

#### **GROUND OF REJECTION TO BE REVIEWED ON APPEAL**

- A. The rejection of claims 1 and 17 under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent 5,512,214 to Koksang.
- B. The rejection of claims 1, 2, 17, 24, and 26 under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent 5,549,880 to Koksang.
- C. The rejection of claims 1-3, 10, 22, and 24-29 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent 5,556,738 to Takamuki et al.

#### **ARGUMENT**

The following argument is organized around the following grouping of claims, which is summarized for the convenience of the Board.

1. Claims 1, 17, 22, 24 and 26 are within a first claim group directed to a collection of metal vanadium oxide particles or batteries formed with metal vanadium oxide particles with the particles having a specified average particles size.
2. Claim 2 is in a second claim group directed to a collection of metal vanadium oxide particles with an average diameter from about 5 nm to about 100 nm.



3. Claim 3 is in a third claim group directed to a collection of metal vanadium oxide particles with an average diameter from about 5 nm to about 50 nm.
4. Claims 10 and 25 are within a fourth claim group directed to a method for producing metal vanadium oxide particles using vanadium oxide particles with a specified average particle size range.
5. Claims 27-29 are within a fifth claim group directed to crystalline metal vanadium oxide.

#### LEGAL AUTHORITY

The Court of Appeals for the Federal Circuit has exclusive appellate jurisdiction for cases arising under the patent law under 28 U.S.C. § 1295 (a)(1). The Federal Circuit has adopted as binding precedent all holdings of its predecessor courts, the U.S. Court of Claims and the U.S. Court of Customs and Patent Appeals. South Corp. v. U.S., 215 USPQ 657 (Fed. Cir. 1982). Therefore, unless they have been overruled en banc, CCPA cases are binding precedent for the present appeal.

#### A. ANTICIPATION

##### 1. A Single Reference Must Disclose Every Element Set Forth In a Claim To Anticipate The Claim

"For a prior art reference to anticipate in terms of 35 U.S.C. § 102, every element of the claimed invention must be identically shown in a single reference. **These elements must be arranged as in the claim under review**, but this is not an 'ipsissimis verbis' test." In re Bond, 15 USPQ2d 1566, 1567 (Fed. Cir, 1990)(Internal citations omitted and emphasis added.).

"If the prior art reference does not expressly set forth a particular element of the claim, that reference still may anticipate if that element is 'inherent' in its disclosure. To establish

inherency, the intrinsic evidence 'must make it clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill. Inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient.'" In re Robertson, 49 USPQ2d 1949, 1950, 1951 (Fed. Cir. 1999), citing Continental Can Co. v. Monsanto Co., 20 USPQ2d 1746, 1749 (Fed. Cir. 1991).

"Every element of the claimed invention must be literally present, arranged as in the claim. **The identical invention must be shown in as complete detail as is contained in the patent claim.**" Richardson v. U.S. Suzuki Motor Corp., 9 USPQ2d 1913, 1920 (Fed. Cir. 1989)(Internal citations omitted, and emphasis added.). "Here, as well, anticipation is not shown by a prior art disclosure which is only 'substantially the same' as the claimed invention." Jamesbury Corp. v. Litton Industrial Products, Inc., 225 USPQ 253, 256 (Fed. Cir. 1985)(emphasis added).

## 2. Ranges

Claims covering a range of composition narrower than a broader range covered in the prior art are not anticipated, although they may be obvious over the prior art. In re Malagari, 182 USPQ 549, 553 (CCPA 1974). Such claims are analogous to the claim of a species or subgenus within a genus, which may be patentable and generally are not obvious. "Anticipation requires a showing that each limitation of a claim is found in a single reference, either expressly or inherently. It is well established that the disclosure of a genus in the prior art is not necessarily a disclosure of every species that is a member of that genus. There may be many species encompassed within a genus that are not disclosed by a mere disclosure of the genus. On the other hand, a very small genus can be a disclosure of each species within the genus." Atofina v. Great Lakes Chem. Corp., 441 F.3d 991, 999, 78 USPQ2d 1417, 1423 (Fed. Cir. 2006).

A prima facie case of obviousness exists if the claimed ranges "overlap or lie inside ranges disclosed by prior art." In re Wertheim, 541 F.2d 257, 191 USPQ 90 (CCPA 1976); In re Woodruff, 919 F.2d 1575, 16 USPQ2d 1934 (Fed. Cir. 1990); In re Geisler, 116 F.3d 1465, 1469-71, 43 USPQ2d 1362, 1365-66 (Fed. Cir. 1997). If the claimed ranges do not overlap with the prior art ranges, a prima facie case of obviousness exists if they are so close that one skilled in the art would have expected them to have the same properties. "[A] prior art reference that discloses a range encompassing a somewhat narrower claimed range is sufficient to establish a prima facie case of obviousness." In re Peterson, 315 F.3d 1325, 1330, 65 USPQ2d 1379, 1382-83 (Fed. Cir. 2003). See also In re Harris, 409 F.3d 1339, 74 USPQ2d 1951 (Fed. Cir. 2005). Based on a fact intensive inquiry, a range may be disclosed in multiple prior art references instead of a single prior art reference. Iron Grip Barbell Co., Inc. v. USA Sports, Inc., 392 F.3d 1317, 1322, 73 USPQ2d 1225, 1228 (Fed. Cir. 2004).

## B. OBVIOUSNESS

### 1. The Examiner Bears The Burden Of Demonstrating Obviousness.

The Applicants note that the patent office has the burden of persuasion in showing that the Applicants are not entitled to a patent. "[T]he conclusion of obviousness vel non is based on the preponderance of evidence and argument in the record." In re Oetiker, 24 USPQ2d 1443, 1445 (Fed. Cir. 1992). The patent office has the ultimate burden of persuasion in establishing that an applicant is not entitled to a patent. Id. at 1447, concurring opinion of Judge Plager. "The only determinative issue is whether the record as a whole supports the legal conclusion that the invention would have been obvious." Id.

"In rejecting claims under 35 U.S.C. §103, the examiner bears the initial burden of presenting a prima facie case of obviousness." In re Rijckaert, 28 USPQ2d 1955, 1956 (Fed. Cir. 1993). If the Examiner fails to establish a prima facie case of obviousness, the obviousness

rejection must be withdrawn as a matter of law. In re Ochiai, 37 USPQ at 1131 ("When the references cited by the examiner fail to establish a prima facie case of obviousness, the rejection is improper and will be overturned"). "If examination at the initial stage does not produce prima facie case of unpatentability, then without more the applicant is entitled to grant of the patent." In re Oetiker, 24 USPQ2d 1443, 1444 (Fed. Cir. 1992).

"Only if that burden is met, does the burden of coming forward with evidence or argument shift to the applicant." In re Rijckaert, 28 USPQ2d at 1956. "After evidence or argument is submitted by the applicant in response to an obviousness rejection, 'patentability is determined on the totality of the record, by a preponderance of the evidence with due consideration to persuasiveness of the argument.'" In re Chu, 36 USPQ2d 1089, 1094 (Fed. Cir. 1995)(quoting In re Oetiker, 24 USPQ2d 1443, 1444 (Fed. Cir. 1992)).

## 2. The References Must Teach Or Suggest All Of The Claim Elements

Prima facie obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. In re Ochiai, 37 USPQ 1127, 1131 (Fed. Cir. 1995). ("The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'") To establish obviousness of a claimed invention, all of the claim limitations must be taught or suggested by the prior art." CFMT, Inc. v. Yieldup Intern. Corp., 349 F.3d 1333 (Fed. Cir. 2003) (citing In re Royka, 490 F.2d 981 (CCPA 1974).

To establish prima facie obviousness, all the elements of the claim must be taught or suggested by the cited references without the benefit of hindsight based on the applicant's own disclosure. "To imbue one of ordinary skill in the art with knowledge of the invention in suit, when no prior art reference or references of record convey or suggest that knowledge, is to fall victim to the insidious effect of a hindsight syndrome wherein that which only the inventor taught is used against its teacher." W. L. Gore & Assocs., Inc. v. Garlock, Inc., 220 USPQ 303, 312-13 (Fed. Cir.

1983). "Skill in the art does not act as a bridge over gaps in the substantive presentation of an obviousness case, but instead supplies the primary guarantee of objectivity in the process." All-Site Corp. v. VSI International Inc., 50 USPQ2d 1161, 1171 (Fed. Cir. 1999).

The Supreme Court has recently clarified that this examination of the teachings of the prior art should not be performed rigidly. It held that "The combination of familiar elements according to known methods is likely to be obvious when it does no more than yield predictable results." KSR Intern. Co. v. Teleflex Inc., 127 S.Ct. 1727, 1739 (2007). Specifically, "a court must ask whether the improvement is more than the predictable use of prior art elements according to their established functions." *Id.* at 1731. "Often, it will be necessary for a court to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person of ordinary skill in the art, all in order to determine whether there was an apparent reason to combine the known elements in the fashion claimed by the patent at issue." *Id.* at 1740. The Court noted that "it can be important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does." *Id.* at 1731. This is so because "inventions [in most, if not all, instances] rely upon building blocks long since uncovered, and claimed discoveries almost of necessity will be combinations of what, in some sense, is already known." *Id.* "Under the correct analysis, any need or problem known in the field of endeavor at the time of invention and addressed by the patent can provide a reason for combining the elements in the manner claimed." *Id.* at 1732. See also *In re Icon Health and Fitness, Inc.*, 83 U.S.P.Q.2d 1746, 2007 WL 2189161.

### 3. The Claimed Recited Properties Of The Claimed Compositions Of Matter Are Claim Elements

It is long established that a composition of matter is indistinguishable from its properties. *In re Papesch*, 137 USPQ 43, 51 (CCPA 1963); *In re Cescon*, 177 USPQ 264, 266 (CCPA 1973).

There are two types of properties, chemical/compositional properties and physical properties. The chemical/compositional properties of the composition of matter determine what the material is, while the physical properties relate to the interaction and behavior of the composition of matter. Often unique or unexpected physical properties are used to establish the existence of an unobvious composition when chemical/compositional properties either are unknown or do not fully represent the unobviousness of the composition. However, discovery of a surprising or unexpected physical property does not necessarily control an obviousness determination, and all the evidence under the Graham factors must be considered. See, for example, Richardson-Vicks v. Upjohn Co., 44 USPQ2d 1181, 1187 (Fed. Cir. 1997). In the present case, the claims do not relate to the discovery of properties of previously known or suggested materials.

Obviousness under 35 U.S.C. §103 must be evaluated by viewing the invention as a whole. In re Langer, 175 USPQ 169, 171 (CCPA 1972). "In effect, we consider the prior art 'as a whole' with the claimed subject matter 'as a whole.'" Id. This rule superseded other principles, and specifically, "homology should not be automatically equated with prima facie obviousness." Id. (emphasis added). "To give meaning to the language of 35 U.S.C. 103 which speaks to the subject matter 'as a whole,' we feel weight must be given the properties of a compound or composition of matter." In re Murch, 175 USPQ 89, 92 (CCPA 1972)(emphasis added).

The present claims are directed to compositions of matter or method for manipulating compositions of matter. Certain claimed aspects of the present invention are chemical/compositional properties that make the material a different composition of matter. In particular, Applicants' **claimed compositions** have several compositional features of particular relevance. First, the composition of matter comprises particles with specified properties. Specifically, the particles have a specified range of average particle sizes. Average particle size is a chemical/compositional property similar to chemical formula or molecular weight of a polymer.

Collections of particles with one average particle size are a different composition of matter and will have different physical properties from collections of particles with other average particle sizes.

Similarly, the distribution of particle sizes is another independent chemical/composition property of solid particles that is distinct from the average particle size. A particle collection with a particular particle size distribution is a different composition of matter and will have different physical properties from other collections of particles with different particle size distributions. Applicants have developed an approach using light/radiation-based pyrolysis to produce the highly uniform powders/particles, which is the subject of some of the present claims. These highly uniform particles can be further reacted to form other product particles with desirable properties. A particle collection with a narrow particle size distribution is more uniform.

4. To Support A Finding Of Obviousness Based On Cited Art, The Cited Art Must Provide A Means Of Obtaining The Claimed Composition Or Apparatus

The proposition is well established that the cited art only renders a composition of matter or apparatus unpatentable to the extent that the cited art enables the disputed claims, in other words, if the cited art provides a means of obtaining the claimed composition or apparatus.

To the extent that anyone may draw an inference from the Von Bramer case that the mere printed conception or the mere printed contemplation which constitutes the designation of a 'compound' is sufficient to show that such a compound is old, regardless of whether the compound is involved in a 35 U.S.C. 102 or 35 U.S.C. 103 rejection, we totally disagree. ... We think, rather, that the true test of any prior art relied upon to show or suggest that a chemical compound is old, is whether the prior art is such as to place the disclosed 'compound' in the possession of the public. In re Brown, 141 USPQ 245, 248-49 (CCPA 1964)(emphasis in original)(citations omitted).

Similarly, see In re Hoeksema, 158 USPQ 596, 600 (CCPA 1968)(emphasis in original):

We are certain, however, that the invention as a whole is the claimed compound and a way to produce it, wherefore appellant's argument has substance. There has been no showing by the Patent Office in this record that the claimed compound can exist because there is no

showing of a known or obvious way to manufacture it; hence, it seems to us that the 'invention as a whole,' which section 103 demands that we consider, is not obvious from the prior art of record.

While there are valid reasons based on public policy as to why this defect in the prior art precludes a finding of obviousness under section 103, *In re Brown*, supra, its immediate significance in the present inquiry is that it poses yet another difference between the claimed invention and the prior art which must be considered in the context of section 103. So considered, we think the differences between appellant's invention as a whole and the prior art are such that the claimed invention would not be obvious within the contemplation of 35 U.S.C. 103.

The Federal Circuit has further emphasized these issues. "But to be prior art under section 102(b), a reference must be enabling. That is, it must put the claimed invention in the hands of one skilled in the art." *In re Sun*, 31 USPQ2d 1451, 1453 (Fed. Cir. 1993)(unpublished). Assertions in a prior art reference do not support an anticipation or obviousness rejection unless the references place the claimed invention in the hands of the public. *Beckman Instruments Inc. v. LKB Produkter AB*, 13 USPQ2d 1301, 1304 (Fed. Cir. 1989). "In order to render a claimed apparatus or method obvious, the prior art must enable one skilled in the art to make and use the apparatus or method." *Id.* While a properly citable reference is prior art for all that it teaches, references along with the knowledge of a person of ordinary skill in the art must be enabling to place the invention in the hands of the public. *In re Paulsen*, 31 USPQ2d 1671, 1675 (Fed. Cir. 1994). See also *In re Donohue*, 226 USPQ 619, 621 (Fed. Cir. 1985).

#### 5. Obviousness Over A Single Prior Art Reference

The importance of the principle that the prior art itself must suggest the motivation to modify the teachings of a reference was eloquently stated in *In re Rouffet*, 47 USPQ2d 1453, 1458 (Fed. Cir. 1998)(emphasis added):

The Board did not, however, explain what specific understanding or technical principle within the knowledge of one of ordinary skill in the art would have suggested the combination. **Instead the board merely invoked the high level of skill in the field of the art. If such a rote invocation could suffice to supply a motivation to combine, the more sophisticated scientific fields would rarely, if ever, experience a patentable technical advance. Instead, in complex scientific**



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Application No. 09/757,519

fields, the Board could routinely identify the prior art elements in an application, invoke the lofty level of skill, and rest its case for rejection. **To counter this potential weakness in the obviousness construct, the suggestion to combine requirement stands as a critical safeguard against hindsight analysis and rote application of the legal test for obviousness.**

Similar principles must be applied when obviousness is based on the teachings of a single cited reference.

In appropriate circumstances, a single prior art reference can render a claim obvious. However, there must be a showing of a suggestion or motivation to modify the teachings of that reference to the claimed invention in order to support the obviousness conclusion. This suggestion or motivation may be derived from the prior art reference itself, from the knowledge of one of ordinary skill in the art, or from the nature of the problem to be solved. **Determining whether there is a suggestion or motivation to modify a prior art reference is one aspect of determining the scope and content of the prior art, a fact question subsidiary to the ultimate conclusion of obviousness.**

Sibia Neurosciences, Inc. v. Cadus Pharmaceutical Corp., 55 USPQ2d 1927, 1931 (Fed. Circuit 2000)(internal citations omitted, emphasis added).

#### ANALYSIS

##### A. REJECTIONS OVER KOKSBANG '214 - First Ground of Rejection

The Examiner rejected claims 1 and 17 under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent 5,512,214 to Koksbang (the Koksbang '214 patent). Applicants respectfully request reconsideration of the rejection based on the following analysis. The Koksbang '214 patent does not prima facie anticipate Applicants' claimed invention.

Claim 1 recites: "A collection of particles comprising metal vanadium oxide, the particles having an average diameter less than about 1 micron." The Examiner asserted that the Koksbang '214 patent "discloses a battery comprising metal vanadium oxide particles (abstract) of 'submicron' size (see column 6, lines 7-8)." The Koksbang '214 patent, however, does not disclose "particles comprising metal vanadium oxide, the particles having an average diameter less than about 1

micron." Col. 6, lines 7 and 8 of the Koksbang '214 patent as cited by the Examiner has been taken out of context. The disclosure relates to vanadium oxide halogens NOT metal vanadium oxide. See col. 5, line 58-col. 6, line 8. Halogens are not metals. Thus, these materials are simply not relevant with respect to Appellant's claims.

Furthermore, the disclosure refers to what the individual size of the particles might be and NOT to the average diameter of the particles. The vague disclosure that "[s]uch particles are of micron or submicron size" does not mean the average diameter of the particles will be less than about 1 micron. The average of these particles that are of micron or submicron size will not necessarily be less than about 1 micron.

Additionally, the Koksbang '214 patent is directed to forming vanadium oxide particles having an average size less than 100 microns, desirably less than 50 microns, and preferably, less than 10 microns. See, for example, col. 4, line 67-col. 5, line 4. The Koksbang '214 patent does not disclose an average particle size of less than about 1 micron, as disclosed and claimed by Applicants. It is well established that a broader range is clearly not anticipated by a narrower range. Additionally, this disclosure of average size of vanadium oxide particles does not relate to metal vanadium oxide particles but relates to commingling of carbon and vanadium oxide particles. Although the abstract and an embodiment of the invention does mention lithium vanadium oxide, it also vaguely discloses that "particle size of the lithium vanadium oxide is on the order of that described earlier in connection with  $V_2O_5$  and  $V_6O_{13}$ ." See, for example, col. 5, lines 29-31. It appears that the lithium vanadium oxide particles formed also have approximately an average size less than 100 microns, desirably less than 50 microns, and preferably, less than 10 microns. As discussed above, this does not amount to disclosing an average particle size of less than about 1 micron.

In summary, the only submicron particles referenced in Koksbang '214 do not refer either to average particle size or even to the materials in Appellant's claims. The vanadium oxide particles,

which also are not metal vanadium oxide particles, are not described with respect to the average particle size of Appellant's claims. Therefore, the Koksbang '214 patent simply does not anticipate Applicants' claimed invention. The Examiner has failed to establish a case of prima facie anticipation. Also, the Examiner has failed to assert any case for obviousness.

In order to render a claimed process obvious, the cited references must place the claimed process in the hands of the public. The Koksbang '214 patent does not disclose how to form vanadium oxide particles with an average particle size less than a micron. The range disclosed in the Koksbang '214 patent is a factor of ten greater than Applicants' claimed average particle size. The Examiner has not indicated how such a reduction in particle size can be performed. While the Koksbang '214 patent disclosed the desirability of having smaller average particle sizes, the Koksbang '214 patent does not indicate that particles with an average particle size less than a micron are achievable. This gap with respect to smaller vanadium oxide particles in the disclosure of the Koksbang '214 patent strongly suggests that Koksbang '214 patent does not enable a person of ordinary skill in the art to form submicron vanadium oxide particles.

In summary, the Koksbang '214 patent simply does not prima facie anticipate Applicants' claimed invention. The Examiner has not indicated any basis for establishing prima facie obviousness. Applicants do not have the burden to establish patentability, although Applicants' do not see any issues within the references of record that call patentability into question.

Since a prima case for anticipation or obviousness has not been established by the Examiner, Applicants respectfully request withdrawal of the rejection of claim 10 under 35 U.S.C. § 102(b) as being anticipated by the Koksbang '214 patent.

**B. REJECTION OVER KOKSBANG '880 - Second Ground of Rejection**

The Examiner rejected claims 1, 2, 17, 24, and 26 under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent 5,549,880 to Koksbang (the Koksbang '880 patent). Applicants respectfully request reconsideration of the rejection based on the following analysis. The Examiner has failed to establish a prima facie case of anticipation. These issues are analyzed in detail in the following.

In a related application 09/606,884, now U.S. Patent 7,214,446, that Examiner applied the same Koksbang '880 patent against claims 47-52, which also involve average diameter of vanadium oxide particles. The assignee of the present application to Appellant appealed the Examiner's rejection of claims 47-52, and a decision was rendered in favor of Applicants, resulting in an allowance of the application. Appellant refers to the attached Opinion by the Board of Patent Appeals and Interferences with Appeal No. 2006-9712.

**Group 1 Claims**

The Patent Office has the burden to establish prima facie unpatentability. The rejection formally presented by the Examiner is based on anticipation, although for completeness, Appellant also addresses obviousness.

The Koksbang '880 patent does not prima facie anticipate Applicants' claimed invention. Specifically, pending claim 1 specifies that the average particle size for the claimed collection of metal vanadium oxide particles is less than a micron. It is further emphasized that in Appeal No. 2006-0712, the Board stated: "As correctly argued by appellants (Brief, pages 8-10; Reply Brief, pages 2 and 3), Koksbang does not disclose or suggest that the range of particle sizes taught is an average size or diameter as required by claim 47 on appeal and the examiner has not convincingly established that the disclosure of Koksbang should be interpreted or construed as an 'average' size or diameter (Answer, page 4)." See page 3. "Furthermore, Koksbang

specifically teaches the criticality of the 'particle size' of the product, disclosing a range of particle sizes but never disclosing or suggesting an average of particle sizes or diameters (col. 2, lines 59-61; col. 5, lines 1-6; and col. 6, lines 56-60). We note that the examiner has not submitted any substantive evidence that the term 'particle size' was known in this art to mean an *average* particle size." See pages 3 and 4.

The Koksbang '880 patent does **not** disclose metal vanadium oxide particles with an average particle size less than a micron either **explicitly or inherently**. The Koksbang '880 patent describes a lithium vanadium oxide, which is a species of metal vanadium oxides, "in the form of a fine powder having a surprisingly small particle size on the order of 0.1 to 5 microns, and typically less than 10 microns." Column 2, lines 59-61. The Koksbang patent **does not identically disclose** the composition of Applicants' invention since the Koksbang patent does not expressly recite that the particle size range disclosed is a range of **average** particle sizes.

Furthermore, it is clear in context that this description of particle sizes is not a description of average particle sizes. In particular, the inclusion of the description of "typically less than 10 microns" is inconsistent with 0.1 to 5 microns being a range of averages. If 0.1 to 5 microns relates to a particular distribution of particle sizes, there is some cut off in the distribution that is used to assign the end points presented. This can be picked, for example, at one standard deviation. Thus, there would be some particles with sizes larger than 5 microns and smaller than 0.1 microns. To then indicate that the particle sizes are typically less than 10 microns would imply that a more stringent criterion is being used to indicate "typically," for example, 90 percent or 95 percent of the particles. This interpretation is perfectly consistent although not explained in the Koksbang patent. So if the "0.1 to 5 microns" is a distribution, the expression "typically less than 10 microns" is not inconsistent. However, if "0.1 to 5 microns" refers to average particle sizes, the expression "typically less than 10 microns" is **inconsistent since a description clearly relating to the distribution would then be contrasted with averages without explanation.**

Since there is no explicit explanation otherwise, the consistent reading of the language in the Koksbang '880 patent is that all values relate to the distribution of particle sizes.

In addition, the Koksbang '880 patent has a **single example** directed to the production of lithium vanadium oxide. A **single set of reaction conditions** are described for the production of the lithium vanadium oxide from column 4, line 49 to 67. "The product was found to have a surprisingly small particle size on the order of 0.1 to 5 microns, and typically less than 10 microns." Column 5, lines 4-6. A **powder product** has a **single average particle size** and a single particle size distribution relating to the characteristics of the particles within the powder. Since the quoted language was used to describe a **single product**, it must be referring to a single distribution of particle sizes that would have a corresponding single average particle size, not a range of average particle sizes. Based on a single example with one set of reaction conditions, the only consistent interpretation of the language in the Koksbang '880 patent is that 0.1 to 5 microns refers to a single distribution with an average particle size of roughly 2.5 microns. Since the single set of particle properties disclosed in the Koksbang '880 patent have an average particle size significantly greater than the claimed particle size, the Koksbang '880 patent does not explicitly disclose a collection of metal vanadium oxide particles with an average particle size less than one micron.

Similarly, the Koksbang '880 patent does not inherently disclose metal vanadium oxide particles with an average particle size less than one micron. Specifically, the Koksbang patent explicitly discloses the particle size of the metal vanadium oxide particles. There are no particle collections in the Koksbang '880 patent with inherent size properties that are not described, so there cannot be inherent disclosure relating to average particle sizes. Since the Koksbang '880 patent does not explicitly or inherently disclose metal vanadium oxide particles with an average particle size less than a micron, the Koksbang '880 patent does not anticipate Applicants' claimed invention.

With respect to obviousness, the Examiner has clearly not stated a prima facie case for obviousness. It is simply not the Applicants' burden to establish patentability. With respect to the Examiner's assertions regarding the possible formation of Applicants' claimed particle from the particles formed by the process of the Koksbang '880 patent, this can only be relevant to an obviousness analysis. However, the Koksbang '880 patent does not teach or suggest any separation techniques. Under well established legal principles, the modification of the teachings of a reference can only be based upon the teachings of another reference or what is well known to a person of ordinary skill in the art. The Examiner has not asserted that appropriate teaching is well known in the art or provided a reference that describes appropriate knowledge being well known in the art. If it was well known to a person of ordinary skill in the art how to form the claimed particle collections from the particle collections described in the Koksbang '880 patent, it should be possible for the Examiner to provide such a reference. Similarly, the Examiner has not asserted or implied in the phone conferences that he has personal knowledge that appropriate approaches are known in the art for performing the requires submicron particle separation.

Cited references must teach all of the claim elements. Specifically, the cited art must place the invention in the hands of the public to support an obviousness or anticipation rejection. The Koksbang '880 patent simply does not put the invention in the hands of the public. Certainly, with respect to Applicants' claimed invention, the Examiner has fallen far short of meeting his burden of establishing prima facie anticipation or obviousness.

If a person of ordinary skill in the art could practice the claimed invention without undue experimentation based on the disclosure in the Koksbang '880 patent, the Examiner should easily be able to support that assertion with some kind of evidence. The Examiner has presented no evidence to support an obviousness rejection over the Koksbang '880 patent.

Since the Examiner has fallen short of establishing prima facie unpatentability of Applicants' claimed invention, the rejection should be withdrawn.

Group 2 Claim

The claims of group 2 relate to collections of metal vanadium oxide particles with an average particle size from 5 nm (0.005 microns) to 100 nm (0.1 microns). As indicated above, the Koksbang '880 patent does not disclose metal vanadium oxide particles with an average particle size of less than about 1 micron, let alone average particle size from 0.005 microns to 0.1 microns. Therefore, the Examiner has failed to establish prima facie anticipation of this claim.

C. REJECTION OVER TAKAMUKI '738 – Third grounds of rejection

The Examiner rejected claims 1-3, 10, 22, and 24-29 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent 5,556,738 to Takamuki et al. (the Takamuki '738 patent). Applicants respectfully request reconsideration of the rejection based on the following analysis. The Examiner has failed to establish a prima facie case of obviousness. The same deficiencies present in the Koksbang '214 patent and the Koksbang '880 patent regarding metal vanadium oxide particles having an average diameter less than about 1 micron are also present in the Takamuki '738 patent.

Also, Examiner rejected dependent claims 22 and 24-29 using the Takamuki '738 patent without rejecting the corresponding independent claim 17 using the Takamuki '738 patent. Applicants respectfully request clarification of the status of claims 17, 22, and 24-29 with respect to the Takamuki '738 patent. Applicants will address claims 17, 22, and 24-29 under the Takamuki '738 patent.

Group 1 Claims

Group 1 claims are directed to "...particles comprising metal vanadium oxide, the particles having an average diameter less than about 1 micron." In the Office Action dated July 16, 2007, Examiner states that "Takamuki '738 discloses fine particles comprising mixed metal



oxide having a particle size (see column 5, lines 21-23) and specifically vanadium pentoxide (see column 5, lines 51 and 52).” Examiner appears to ignore that particles comprising metal vanadium oxide must not only contain vanadium atom(s) but also metal non-vanadium atom(s) in the oxide composition as disclosed in the specification. In other words, particles comprising metal vanadium oxide have a composition of  $M_xV_yO_z$ , where M refers to a non-vanadium metal atom and where x, y, and z describe the stoichiometry. Vanadium pentoxide ( $V_2O_5$ ) is NOT a metal vanadium oxide because it is missing the non-vanadium metal atom. A metal vanadium oxide composition does not refer either to physical blends of different particles or to coatings on particles. The claimed invention refers to a particular composition of matter that is formed into particles with the claimed average particle size. Applicants do not acquiesce that Takamuki teaches an oxide at all since in some contexts metal oxide “sols” refers to hydrated or hydroxide forms of the materials. Since Takamuki clearly does not teach a metal vanadium oxide, this issue is moot.

Examiner also states that “Takamuki fails to specifically disclose an average diameter of less than about 1 micron.” Examiner stated that it’s obvious by citing to Takamuki’s disclosure of “mixed metal oxide having a particle size of 1-300 (see column 5, lines 21-23) and specifically 30 nm for vanadium pentoxide (see column 5, lines 51 and 52), and a gelatin shell of 1-500 nm which is previously cross-linked to increase miscibility (see column 5, lines 58-60, 65, 66).” These citations of Takamuki fail to disclose metal vanadium oxide particles with an average diameter of less than about 1 micron. Column 5, lines 21-23 is not directed to metal vanadium oxide particles. Column 5, lines 51 and 52 is also not directed to metal vanadium oxide particles. Column 5, lines 58-60 is not directed to either metal vanadium oxide particles or particle size but the thickness of a gelatin shell. Not only do these citations fail to disclose the claimed invention, Examiner failed to provide a reason for modifying these citations to the claimed invention of metal vanadium oxide particles with an average diameter of less than about

1 micron (e.g. Examiner failed to provide a secondary reference that makes up for the deficiencies of Takamuki). Thus, the Examiner has failed to establish prima facie obviousness of the Group 1 claims.

#### Group 3 Claim

The claim of group 3 relate to collections of metal vanadium oxide particles with an average particle size from 5 nm (0.005 microns) to 50 nm (0.05 microns). As indicated above, the Takamuki '738 patent does not disclose metal vanadium oxide particles with an average particle size of less than about 1 micron, let alone average particle size from 0.005 microns to 0.05 microns. Thus, the Examiner has failed to establish prima facie obviousness of the Group 3 claim.

#### Group 4 Claims

Group 4 claims is directed to "[a] method of producing particles of metal vanadium oxide comprising heating a mixture of vanadium oxide particles with a non-vanadium metal compound, the vanadium oxide particles having an average diameter less than about 1 micron." In the Office Action dated July 16, 2007, Examiner basically repeated his rejection for claim 1 only to add that "wherein the particles are mixed at a temperature of 30-80 degrees Celsius." Examiner completely ignores the step of heating vanadium oxide particles with a non-vanadium metal. Col. 5, lines 51 and 52 as cited by the Examiner discloses vanadium pentaoxide, which is an example of inorganic fine particles used in Takamuki's invention. Takamuki also discloses mixing a gelatin aqueous solution and an aqueous dispersion of inorganic fine particles, gradually adding a cross-linking agent, and stirring at a temperature of 30-80 degrees Celsius. Col. 6, lines 12-18. Takamuki discloses heating a vanadium oxide with a gelatin or cross-linking agent NOT a non-vanadium metal compound. Also, as indicated above, Examiner states that

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the limitation of average diameter of less than about 1 micron is obvious without providing any teaching, motivation, or suggestion. Thus, the Examiner failed to establish prima facie obviousness of group 4 claims.

#### Group 5 Claims

Claims are directed to crystalline metal vanadium oxide. Examiner states that it's obvious because "Takamuki disclose both tabular and crystal grains (column 3, lines 19-22)." The crystal grains are directed to silver halides regarding the growth of silver halides and achieving high sensitivity. Takamuki does not disclose crystalline metal vanadium oxide. As indicated above, Takamuki fails to disclose particles comprising metal vanadium oxide. Also indicated above, Examiner states that the limitation of average diameter of less than about 1 micron is obvious without providing any teaching, motivation, or suggestion. Thus, the Examiner failed to establish prima facie obviousness of Group 5 claims.

#### Summary

The Examiner has failed to meet his burden of establishing prima facie unpatentability of Applicants' claimed invention based on the Koksang '214 patent, the Koksang '880 patent, and the Takamuki '738 patent. Applicants respectfully request withdrawal of the rejection of claims 1-3, 10, 17-22, and 24-29.

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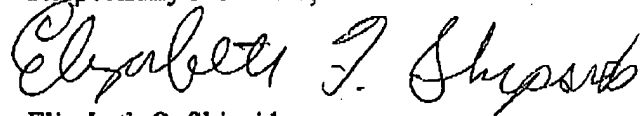
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Application No. 09/757,519

CONCLUSIONS AND REQUEST FOR RELIEF

Applicants submit that claims 1-3 and 6-29 are in condition for allowance. Thus, Applicants respectfully request the reversal of the rejections of claims 1-3, 10, 17-22, and 24-29 and the allowance of claims 1-3 and 6-29.

Respectfully submitted,



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**APPEALED CLAIMS APPENDIX**

1. A collection of particles comprising metal vanadium oxide, the particles having an average diameter less than about 1 micron.
2. The collection of particles of claim 1 wherein the particles have an average diameter from about 5 nm to about 100 nm
3. The collection of particles of claim 1 wherein the particles have an average diameter from about 5 nm to about 50 nm.
- 4-5. (Cancelled)
6. The collection of particles of claim 1 wherein less than about 1 particle in  $10^6$  have a diameter greater than about four times the average diameter of the collection of particles.
7. The collection of particles of claim 1 wherein less than about 1 particle in  $10^6$  have a diameter greater than about two times the average diameter of the collection of particles.
8. The collection of particles of claim 1 wherein the collection of particles have a distribution of particle sizes such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

9. The collection of particles of claim 1 wherein the collection of particles have a distribution of particle sizes such that at least about 95 percent of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.
10. A method of producing particles of metal vanadium oxide comprising heating a mixture of vanadium oxide particles with a non-vanadium metal compound, the vanadium oxide particles having an average diameter less than about 1 micron.
11. The method of claim 10 wherein the vanadium oxide particles have an average diameter from about 5 nm to about 100 nm.
12. The method of claim 10 wherein the non-vanadium metal compound comprises silver nitrate.
13. The method of claim 10 wherein the vanadium oxide particles comprise crystalline  $V_2O_5$ .
14. The method of claim 10 wherein the heating is performed at a maximum temperature from about 200°C to about 330°C.
15. The method of claim 10 wherein the heating is performed at a maximum temperature from about 200°C to about 300°C.
16. The method of claim 10 wherein the heating is performed for less than about 20 hours.

17. A battery comprising a positive electrode having active particles comprising metal vanadium oxide within a binder, the active particles having an average diameter less than about 1 micron.

18. The battery of claim 17 wherein the active particles have an average diameter from about 5 nm to about 100 nm.

19-21. (Cancelled)

22. The battery of claim 17 wherein the positive electrode further comprises supplementary, electrically conductive particles.

23. The battery of claim 17 wherein less than about 1 active particle in  $10^6$  have a diameter greater than about four times the average diameter of the collection of active particles.

24. The collection of particles of claim 1 wherein the particles have an average diameter less than about 500 nm.

25. The method of claim 10 wherein the vanadium oxide particles having an average diameter less than about 500 nm.

26. The battery of claim 17 wherein the active particles have an average diameter less than about 500 nm.

27. The collection of particles of claim 1 wherein the metal vanadium oxide is crystalline.

28. The method of claim 10 wherein the metal vanadium oxide is crystalline.
29. The battery of claim 17 wherein the metal vanadium oxide is crystalline.



**EVIDENCE APPENDIX**

A - U.S. Patent 5,549,880 to Koksang was filed by the Applicant in an Information Disclosure Statement on April 30, 2001 but received by the USPTO on May 4, 2001 and considered by the Examiner on June 27, 2001. This patent was cited by the Examiner in subsequent Office Actions beginning with the Office Action dated July 7, 2001.

B - U.S. Patent 5,512,214 to Koksang was first cited by the Examiner in an Office Action dated August 8, 2002.

C - U.S. Patent 5,556,738 to Takamuki was first cited by the Examiner in an Office Action dated February 7, 2007.



US005549880A

# United States Patent [19]

## Koksbang

[11] Patent Number: 5,549,880  
 [45] Date of Patent: Aug. 27, 1996

### [54] METHOD OF MAKING LITHIUM-VANADIUM-OXIDE ACTIVE MATERIAL

[76] Inventor: Rene Koksbang, 4231 Norwalk Dr.,  
San Jose, Calif. 95129

[21] Appl. No.: 221,301

[22] Filed: Mar. 31, 1994

[51] Int. Cl.<sup>6</sup> C01G 31/00; H01M 4/58;  
C01D 15/02

[52] U.S. Cl. 423/593; 429/218

[58] Field of Search 423/593; 429/218

### [56] References Cited

#### U.S. PATENT DOCUMENTS

3,063,795	11/1962	Smith	23/51
3,063,796	11/1962	Kelmers	23/51
3,728,442	4/1973	Pukhomov et al.	423/592
4,061,711	12/1977	Morgan et al.	423/67
4,119,707	10/1978	Thorne et al.	423/592
4,543,341	9/1985	Barringer et al.	423/593
4,636,248	1/1987	Ogata et al.	423/593
4,830,939	5/1989	Lee et al.	429/192
4,879,190	11/1989	Lundsgaard	429/94
4,918,035	4/1990	Inoue et al.	423/593
4,920,093	4/1990	Nonaka et al.	423/593
4,990,413	2/1991	Lee et al.	429/191
5,013,620	5/1991	Miyazaki et al.	429/194
5,023,071	6/1991	Sherif	423/593
5,037,712	8/1991	Shackle et al.	429/192
5,229,225	7/1993	Shackle	429/191
5,326,545	7/1994	Koksbang et al.	423/593

5,334,334 8/1994 Koksbang 423/593

#### FOREIGN PATENT DOCUMENTS

0397608	11/1990	European Pat. Off.	
62-143825	6/1987	Japan	423/593
63-112420	5/1988	Japan	423/593
2-233505	9/1990	Japan	423/593
3-170305	7/1991	Japan	423/593
94/23461	10/1994	WIPO	

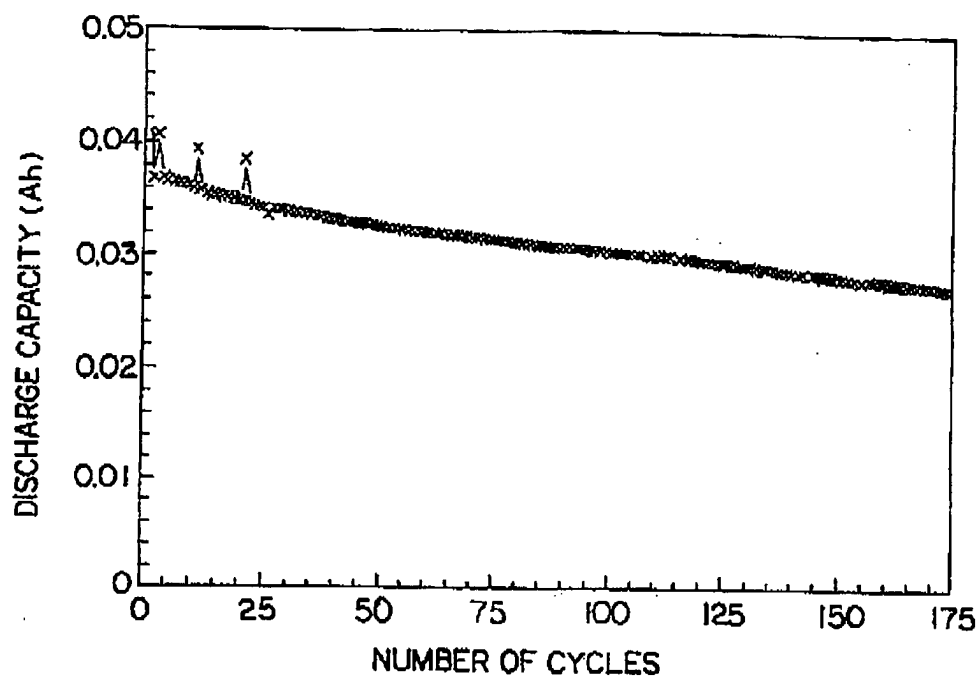
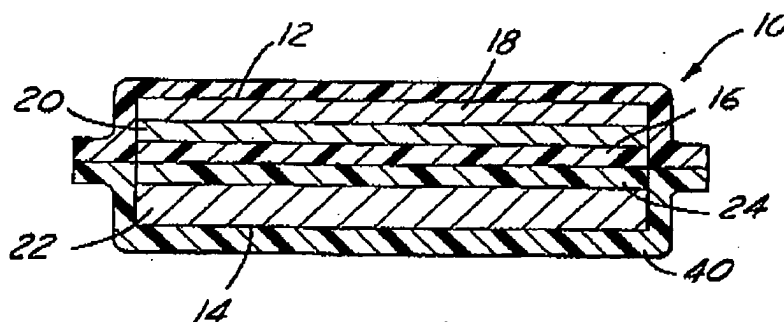
Primary Examiner—Charles L. Bowers, Jr.

Assistant Examiner—J. Pasterczyk

### [57] ABSTRACT

A method of making an electrode active material of the nominal general formula  $\text{LiV}_y\text{O}_z$  where y is greater than 0 and up to about 3 and z is greater than 0 and up to about 8, comprises a series of steps. In the first step, lithium hydroxide is dispersed in an alcohol of the general formula  $\text{C}_n\text{H}_{2n+1}\text{OH}$ . The alcohol and the hydroxide are each in an amount sufficient to provide a lithium alkoxide of the general formula  $\text{LiOC}_n\text{H}_{2n+1}$ . Next, progressive amounts of an oxide of vanadium having the general formula  $\text{V}_2\text{O}_5$  (vanadium pentoxide) are added while stirring the mixture. The amount of vanadium pentoxide in the mixture is sufficient to provide about 3 moles of vanadium for each mole of lithium present in the alkoxide. Then, the mixture is heated to an elevated temperature for a time sufficient to change the color of the oxide of vanadium and provide a solid precipitate. The solid precipitate is separated from the mixture and dried to obtain a powder of an oxide of vanadium having the nominal general formula  $\text{LiV}_y\text{O}_z$ ,  $0 < y \leq 3$  and  $0 < z \leq 8$ .

16 Claims, 1 Drawing Sheet

**U.S. Patent****Aug. 27, 1996****5,549,880****FIG. 1****FIG. 2**

5,549,880

# 1

## METHOD OF MAKING LITHIUM-VANADIUM-OXIDE ACTIVE MATERIAL

### FIELD OF THE INVENTION

This invention relates to electrochemical batteries, and more particularly to improved positive electrode active material mainly composed of an oxide of vanadium.

### BACKGROUND OF THE INVENTION

Lithium-based cells or batteries often comprise cathodes of transition metal oxides which are used as intercalation compounds. The intercalation reaction involves the interstitial introduction of a guest species, namely lithium, into the host lattice of the transition metal oxide, essentially without structural modification of the host lattice. Such an intercalation reaction is essentially reversible because suitable transition states are achieved for both the forward and reverse of the intercalation reaction.

The basic components of a lithium cell typically include a lithium anode, a separator, and a metal oxide intercalation cathode active material such as a vanadium oxide compound. The cathode is usually a mixture of such an oxide compound and other components such as graphite and an electrolyte/binder which provide ionic transport. During cell operation, incorporation of lithium in the metal oxide occurs.

Current batteries contain high surface area active material such as vanadium oxide and lithium vanadium oxide powders (i.e.  $V_2O_5$ ,  $LiV_2O_5$  and  $LiV_3O_8$ ). These oxide powders are obtained, for example, by milling of vanadium oxide material. Current methods for the manufacture of powders involve mechanical grinding of vanadium oxide material prepared, for example, by rapid quench of molten material or by precipitation from an aqueous solution.

U.S. Pat. No. 5,013,620 describes solid state synthesis of  $Li_{1-x}V_3O_8$  obtained by high temperature melting (at least  $700^\circ\text{C}$ .) of  $V_2O_5$  with  $Li_2CO_3$ , in suitable proportions. The melt, once cooled, gives rise to solid lumps of material which are then difficult to crush and mill in order to obtain the cathode material. In addition, there is reaction between the molten  $LiV_3O_8$  product and most containers which causes contamination of the product.

Formation of an oxide of vanadium in an aqueous solution of lithium hydroxide produces a gel product which is difficult to filter and dry. The dried product is in the form of lumps which are difficult to grind.

As can be seen, present processes produce vanadium oxide in the form of lumps. By standard milling techniques it is difficult to reduce the lumps to a size less than 100 micrometers (microns) and extremely difficult to achieve closer to 10 microns. Smaller vanadium oxide particle sizes are desirable because the larger the surface area, the higher is the current drawn from a battery while the current density on the surface of the vanadium oxide active material remains low which allows high utilization of the active material. A typical coarse  $V_2O_5$  powder of 95% purity available from Fisher Scientific Company, has a median particle size of about 110 microns and a surface area of about 5 meters<sup>2</sup>/gram. Such a powder would need extensive milling.

Therefore, what is needed is a new process of forming a vanadium oxide based active material which does not produce lumps and which is readily adaptable to large scale production.

# 2

## SUMMARY OF THE INVENTION

In accordance with the invention, a method of making an electrode active material of the nominal general formula  $LiV_yO_z$  where y is greater than 0 and up to about 3 and z is greater than 0 and up to about 8, comprises a series of steps. In the first step, lithium hydroxide is dispersed in an alcohol of the general formula  $C_nH_{2n+1}OH$ . The alcohol and the hydroxide are each in an amount sufficient to provide a lithium alkoxide of the general formula  $LiOC_nH_{2n+1}$ . Next, progressive amounts of an oxide of vanadium having the general formula  $V_2O_5$  (vanadium pentoxide) are added while stirring the mixture. The amount of vanadium pentoxide in the mixture is sufficient to provide about 3 moles of vanadium for each mole of lithium present in the alkoxide. Then, the mixture is heated to an elevated temperature for a time sufficient to change the color of the oxide of vanadium and provide a solid precipitate. The solid precipitate is separated from the mixture and dried to obtain a powder of an oxide of vanadium having the nominal general formula  $LiV_yO_z$ ,  $0 < y \leq 3$  and  $0 < z \leq 8$ . It should be noted that the value of z may slightly exceed 8 and be on the order of 8.1 but it is less than 9; and the value of y may exceed 3 but it is less than 4. Accordingly, the nominal formula remains as above.

It is preferred that the mixture contains a stoichiometric amount of the alkoxide and pentoxide. This corresponds to about 2 moles of the alkoxide for each 3 moles of vanadium pentoxide. The stoichiometric mixture is heated to elevated temperature in a range of about  $70^\circ$  to about  $80^\circ$  centigrade, for about one to about three hours. The progress of the reaction  $LiOC_nH_{2n+1} + V_2O_5 \rightarrow LiV_yO_z$  is monitored by observing a color change from yellow/red to brown/black.

Finally, the precipitate is separated from the mixture and is dried at a temperature of about  $110^\circ$  centigrade. A higher temperature, such as  $150^\circ\text{C}$ , may be used but it is not necessary.

Alcohols which are suitable for forming the lithium alkoxide include methanol, ethanol, propanol, butanol, isopropanol, and higher alcohols. The higher alcohols are likely to react more slowly with the lithium. Ethanol is preferred. When ethanol is used, the lithium hydroxide and ethanol provide a lithium alkoxide of the general formula  $LiOCH_2CH_3$  (lithium oxylate or lithium ethoxylate) according to the reaction  $LiOH + CH_3CH_2OH \rightarrow LiOCH_2CH_3 + H_2O$ . Vanadium pentoxide is added to the lithium alkoxide in an amount to provide about 3 moles of vanadium for each mole of lithium. Next, the mixture is heated to the elevated temperature for a time sufficient to react the vanadium pentoxide with the  $LiOCH_2CH_3$  until a color change demonstrates the desired product (precipitate) has been formed. The color change is the same as described above. All other steps of the process are according to the general method described earlier. In one embodiment, the ethanol is present in a solution of 96% ethanol; about 0.5 mole of lithium hydroxide is used for each 200 milliliters of 96% ethanol; and about 0.75 mole of vanadium pentoxide is used for each 0.5 mole of lithium hydroxide.

The  $LiV_yO_z$  product of the invention is in the form of a fine powder having a surprisingly small particle size on the order of 0.1 to 5 microns, and typically less than 10 microns.

The cathode material of the invention was tested in a cell to determine the behavior of specific capacity at an increasing number of charge and discharge cycles.

The rate capability and cycling capacity was markedly improved over lithium vanadium oxide prepared by conventional methods.

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It is an object of the invention to provide a new method for preparing a lithium vanadium oxide positive electrode active material for a lithium battery. Another object is to provide a lithium battery having good charge and discharge capacity. Another object is to provide an improved electrochemical battery based on lithium which maintains its integrity over prolonged life cycle as compared to presently used batteries. Another object is to provide good conversion of the starting materials to the lithium vanadium oxide product.

These and other objects, features and advantages will become apparent from the following description of the preferred embodiments, claims and accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

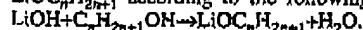
FIG. 1 shows the behavior of the specific capacity at an increasing number of charge and discharge cycles.

FIG. 2 is an illustration of a cross-section of a thin battery, or cell embodying the invention.

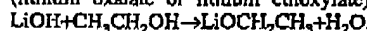
#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

##### I. Preparation of Active Material

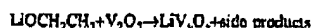
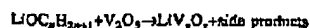
In one embodiment a positive electrode material of the nominal general formula  $\text{LiV}_x\text{O}_y$  is prepared by a series of steps beginning with forming a mixture of lithium hydroxide dispersed in an alcohol of the general formula  $\text{C}_n\text{H}_{2n+1}\text{OH}$ . This produces a lithium alkoxide of the general formula  $\text{LiOC}_n\text{H}_{2n+1}$  according to the following general reaction:



The above reaction may be conducted under room temperature conditions, at a temperature in a range of about 15° to about 95° centigrade, and preferably 70° to 85° C. In accordance with the general formula shown above, one mole of the lithium hydroxide is reacted with one mole of an alcohol to form one mole of the lithium alkoxide product. Alcohols which are suitable for forming the lithium alkoxide include methanol, ethanol, propanol, butanol, isopropanol, and high alcohols. The higher alcohols are likely to react more slowly with the lithium. Ethanol is preferred. In the case of ethanol, the reaction to form the lithium alkoxide (lithium oxalate or lithium ethoxylate) is according to:



The reaction proceeds rather quickly in about a few minutes. Once the lithium alkoxide is formed, to the mixture is added progressive amounts of an oxide of vanadium, having the general formula  $\text{V}_2\text{O}_5$  (vanadium pentoxide). The vanadium pentoxide is added progressively while stirring the mixture so as to provide about three moles of vanadium in the final product for each mole of lithium. This corresponds to a stoichiometric molar ratio of lithium alkoxide to vanadium pentoxide of about 2 to 3. This mixture is heated to a temperature higher than room temperature and preferably in a range of about 70 to about 80 degrees centigrade. Heating is conducted for at least about one half hour and preferably for about one to three hours. In order to react the lithium alkoxide with the vanadium pentoxide according to the following general formulas:



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The progress of the reaction may be followed by observing a change in color whereby the vanadium pentoxide is transformed to a lithium-vanadium oxide product and changes from a yellow-red to a brown-black. The reaction product is the brown to black solid precipitate which is separated and dried to obtain a fine powder of an oxide of the lithium-vanadium oxide having the nominal general formula  $\text{LiV}_x\text{O}_y$  where y is greater than 0 and less than or equal to about 3 and x is greater than 0 and less than or equal to about 8. The drying may occur at a temperature in a range of about 20° to about 300° centigrade. It is preferred that the drying temperature be 110° centigrade. Higher temperatures are not strictly necessary but may be more efficient.

##### Example

The method of the invention was demonstrated by using lithium hydroxide, 96% ethanol, and vanadium pentoxide powder ( $\text{V}_2\text{O}_5$ ).

Vanadium pentoxide of the general formula  $\text{V}_2\text{O}_5$  was obtained from Kerr McGee, Johnson Matthey or Alpha Products of Danvers, Mass. It had a melting point of 690° C., decomposed at 1750° C. and had a specific gravity of 3.357 grams per cc at 18° C. It was a yellow to red crystalline powder. Vanadium pentoxide has a CAS number of 1314-62-1.

Alternatively, the vanadium pentoxide may be prepared from ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ). The ammonium metavanadate is heated to a temperature of about 400° C. to about 450° C. to decompose it to vanadium pentoxide ( $\text{V}_2\text{O}_5$ ), usually in a crystalline form (in the presence of oxygen). The ammonium metavanadate is a solid crystalline material, usually a white to yellow powder. Processes for production of ammonium metavanadate are known in the art and will not be repeated here. Such processes are described in U.S. Pat. Nos. 3,063,795 and 3,063,796; and processes for preparation of ammonium metavanadate and then for production of vanadium pentoxide therefrom are described in U.S. Pat. Nos. 3,728,442, 4,061,711 and 4,119,707, each of which is incorporated by reference in its entirety.

Lithium hydroxide is a powder of essentially colorless crystals having a specific gravity of approximately 2.54 and a melting point of approximately 462° centigrade. In this example, approximately 12 grams of lithium hydroxide was dispersed in about 200 milliliters of 96% ethanol. The 12 grams of lithium hydroxide corresponds to approximately 0.5 mole.

The lithium hydroxide was dissolved in the alcohol to provide the lithium alkoxide. Next, progressive amounts of vanadium pentoxide were added to the mixture containing the lithium alkoxide while keeping the whole mixture stirred. In this example, approximately 136.5 grams of vanadium pentoxide was used which corresponds to about 0.75 mole.

The mixture was then heated to a temperature in a range of approximately 70° to 80° centigrade for about one to three hours. The progress of the reaction was monitored by a color change from the typical yellow/red  $\text{V}_2\text{O}_5$  color to a darker color which was reddish-brown to brown-black. Since monitoring of a color change may be somewhat subjective, it is sufficient to follow the color change, typically from relatively light to a relatively darker color. The color changes are dependent on several factors including the reaction chemistry, particle size, particle morphology, and impurities. Other color changes may be observed besides those described above. The product after filtering and drying,

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however, will typically appear as a brown-black color. The solid precipitate product of the invention was filtered and dried producing a fine powder of the above-mentioned brown-black color. The product was found to have a surprisingly small particle size on the order of 0.1 to 5 microns, and typically less than 10 microns.

The vanadium pentoxide is typically at least partially dissolved in the mixture. Typically, some portion of the vanadium pentoxide is dissolved and some is dispersed in the mixture. It is usually not necessary to use excess amounts of the alkoxide or the pentoxide to drive the reaction to completion. Close to stoichiometric amounts are sufficient and prevent unnecessary waste. It may become necessary in some situations to use an excess amount of the alcohol in order to keep the mixture from becoming solid before the reactions are complete. For example, a two to one ratio of alcohol to lithium hydroxide prevents the formation of a solid lump of  $\text{CH}_3\text{CH}_2\text{OLi}$ . Alternatively, it is possible to use a relatively low concentration of alcohol in water solution, i.e., 50% ethanol rather than 96% ethanol to achieve the same purpose. It is preferred to conduct the drying step in an essentially oxygen-free atmosphere such as under an inert gas, argon, helium, nitrogen, or under a vacuum or subatmospheric pressure. Although it is not thought to be necessary, it is possible to also conduct the reaction step in a similar atmosphere. It is preferred to use linear alcohols in the process, however, branched alcohols may also be used. The lower the alcohol and the less is the branching, the faster the reaction rate one expects. Ethanol is the first choice, With methanol being the second choice.

## II. Preparation of Cell Using Active Material

The cathode active material of the invention is used to prepare cathodes for lithium based electrochemical cells. The cycling performance of the active material (FIG. 1) was obtained using a cell as shown in FIG. 2. The test cell used to determine capacity had an active area of about 28  $\text{cm}^2$ . Referring to FIG. 2, an electrochemical cell or battery 10 has a negative electrode side 12, a positive electrode side 14, and a separator 16 there-between. In accordance with common usage, a battery may consist of one cell or multiple cells. The negative electrode is the anode during discharge, and the positive electrode is the cathode during discharge. The negative electrode side includes current collector 18, typically of nickel, iron, stainless steel, and/or copper foil, and a body of negative electrode material 20. The negative electrode material 20 is sometimes simply referred to as the negative electrode or negative electrode composition. The negative electrode side 12 may consist of only a metallic electrode 20 without a separately distinguishable current collector 18. The positive electrode side 14 includes current collector 22, typically of aluminum, nickel, iron, stainless steel, and/or copper foil, or such foils having a protective conducting coating foil, and a body of positive electrode material 24. The cathode composition 24 has a typical composition as set forth in Table 1 and includes the  $\text{LiV}_2\text{O}_5$  of the invention as the active material. The positive electrode material 24 is sometimes simply referred to as the positive electrode or positive electrode composition. The separator 16 is typically a solid electrolyte or electrolyte separator. Suitable electrolyte separators (polymer electrolyte) are described in U.S. Pat. Nos. 4,830,939, 4,990,413, 5,037,712, and 5,229,225 each of which is incorporated herein by reference in its entirety. The electrolyte separator is a solid organic polymer matrix containing an ionically conducting powder or liquid with an alkali metal salt and the liquid is

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an aprotic polar solvent. Cell 10 also includes a protective covering (not shown) which functions to prevent water and air from contacting the reactive layers of the cell 10.

Cell 10 is preferably a laminar thin cell type including a lithium anode (negative electrode 20). Laminar thin-cell batteries containing lithium anodes are known in the art, and it will be appreciated that the cell can include various constructions such as bi-faced or bi-polar cell designs. Examples of cell constructions include a "jelly roll" or a fan folded laminate strip design as described in U.S. Pat. No. 4,879,190 incorporated herein by reference in its entirety.

Because the cell utilizes a lithium anode layer 20, it is necessary to manufacture the cell in a water (humidity) free environment. Lithium is extremely reactive with water and if reacted, a passivation layer can form on the surface of the anode layer, reducing the efficiency of the layer, and increasing cell impedance. Accordingly, it is particularly desirable to manufacture the cell in an environment having a relative humidity at room temperature of less than 2% (less than 300 ppm water). An environment containing between 1 ppm and 50 ppm water, and preferably less than 1 or 2 ppm water, produces a particularly efficient cell.

TABLE 1

TYPICAL CATHODE COMPOSITION	PERCENT WEIGHT
Active Material $\text{LiV}_2\text{O}_5$	45.0
Carbon	10.0
Propylene Carbonate (PC)	33.0
Poly(ethylene Oxide) (PEO)	1.0
Poly(ethylene Glycol) DiAcrylate (PEGDA)	9.0
TriMethylPoly(ethylene Oxide) Tri-Acrylate (TMPEOTA)	2.0

The cathode composition containing the active material of the invention is coated onto nickel foil, followed by electron beam curing (cross-linking/polymerization) of the acrylate component. Then the electrolyte is coated on top of the cathode and cured with ultraviolet light. The lithium electrode is applied on top of the electrolyte separator and the battery is finally placed in a flexible pouch 40 which is heat sealed under vacuum.

The cathode material of the invention was tested in a cell to determine the behavior of specific capacity at an increasing number of charge and discharge cycles.

The rate capability and cycling capacity was markedly improved over lithium vanadium oxide prepared by conventional methods. The improved behavior of the specific capacity at an increasing number of charge and discharge cycles is as shown in FIG. 1.

Although not wishing to be held to any particular theory, it is thought that the product of the invention is in the form of  $\text{LiV}_2\text{O}_5$  with perhaps a small amount of  $\text{LiV}_3\text{O}_8$ . Hence, the product  $\text{LiV}_2\text{O}_5$ , 0.05-3 and 0.2-58 encompasses both the  $\text{LiV}_2\text{O}_5$  and  $\text{LiV}_3\text{O}_8$ . The product of the invention is preferred compared to other lithium vanadium oxide particles because of the small particle size. In an as-synthesized condition the product is a powder with particle size on the order of 10 microns or less and is easily crushed to a smaller size during the formation of the cathode mixture. The fineness of the particles is important to good performance of the cathode itself because many advantages are obtained. They include no breaking of large particles which typically occurs during intercalation/disintercalation cycles; no contact loss occurs; better contact between the active material and the conductive material (carbon) so it is possible to

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apply high current; and the electrolyte can reach into innermost portions of the cathode to reduce polarization. Such advantages are evidenced by the cycling performance shown in FIG. 1.

The invention provides a lithium vanadium oxide compound having high purity, and good energy, power and cycling capability. The process of the invention is efficient and readily adaptable to continuous production of large quantities of active material in a manufacturing setting.

While this invention has been described in terms of certain embodiments thereof, it is not intended that it be limited to the above description, but rather only to the extent set forth in the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined in the appended claims.

We claim:

1. A method of making an electrode active material of the nominal general formula  $\text{LiV}_y\text{O}_z$  where  $y$  is greater than 0 but less than or equal to 3, and  $z$  is greater than 0 but less than or equal to 8, comprising:

a. forming a mixture of lithium hydroxide dispersed in a alcohol of the general formula  $\text{C}_n\text{H}_{2n+1}\text{OH}$ , each of said lithium hydroxide and said alcohol being provided in an amount sufficient to provide a lithium alkoxide of the general formula  $\text{LiOC}_n\text{H}_{2n+1}$ ;

b. adding to the mixture of step (a) progressive amounts of an oxide of vanadium having the general formula  $\text{V}_2\text{O}_5$  (vanadium pentoxide) while stirring the mixture;

c. reacting the vanadium oxide with the alkoxide in the mixture of step (b) for a time sufficient to provide a solid precipitate of the general formula  $\text{LiV}_y\text{O}_z$ ; and

d. separating and drying the solid precipitate of step (c) to obtain a powder of an oxide of vanadium having the nominal general formula  $\text{LiV}_y\text{O}_z$  where  $0 < y \leq 3$  and  $0 < z \leq 8$ .

2. The method according to claim 1 wherein the mixture of step (b) includes 2 moles of the alkoxide for each 3 moles of vanadium pentoxide.

3. The method according to claim 1 wherein the reacting step (c) is monitored by observing color change as the precipitate is formed.

4. The method according to claim 1 wherein the reaction temperature of step (c) is in a range of 70° to 85° centigrade.

5. The method according to claim 4 wherein the reaction temperature of step (c) is maintained for one half to three hours.

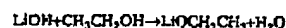
6. The method according to claim 1 wherein the drying step is conducted at a temperature of 110° to 150° centigrade.

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7. The method according to claim 1 wherein the alcohol is selected from the group consisting of methanol and ethanol.

8. A method of making an electrode active material of the general formula  $\text{LiV}_y\text{O}_z$ , where  $y$  is greater than 0 but less than or equal to 3, and  $z$  is greater than 0 but less than or equal to 8, comprising:

a. forming a mixture of lithium hydroxide dispersed in ethanol each in an amount sufficient to provide a lithium alkoxide of the general formula  $\text{LiOCH}_2\text{CH}_3$  according to the reaction



b. adding to the mixture of step (a) progressive amounts of an oxide of vanadium having the general formula  $\text{V}_2\text{O}_5$  (vanadium pentoxide) while stirring the mixture;

c. reacting the oxide of vanadium with the  $\text{LiOCH}_2\text{CH}_3$  in the mixture of step (b) for a time sufficient to provide a solid precipitate of the general formula  $\text{LiV}_y\text{O}_z$ ; and

d. separating and drying the solid precipitate of step (c) to obtain a powder of an oxide of vanadium having the nominal general formula  $\text{LiV}_y\text{O}_z$  where  $0 < y \leq 3$  and  $0 < z \leq 8$ .

9. The method according to claim 8 wherein the ethanol is present in a solution of at least 50% ethanol.

10. The method according to claim 8 wherein 96% ethanol is used and 0.5 moles of lithium hydroxide are used for each 200 milliliters of 96% ethanol.

11. The method according to claim 8 wherein 0.75 moles of vanadium pentoxide are used in step (b) for each 0.5 moles of lithium hydroxide used in step (a).

12. The method according to claim 8 wherein the mixture of step (b) includes 2 moles of the alkoxide of step (a) for each 3 moles of vanadium pentoxide.

13. The method according to claim 8 wherein reacting step (c) is monitored by observing color change as the precipitate is formed.

14. The method according to claim 8 wherein the reaction temperature of step (c) is in a range of about 70° to 85° centigrade.

15. The method according to claim 14 wherein the reaction temperature of step (c) is maintained for one half to three hours.

16. The method according to claim 8 wherein the drying step is conducted at a temperature of about 110° centigrade.

\* \* \* \* \*



US005512214A

# United States Patent [19] Koksbang

[11] Patent Number: **5,512,214**  
[45] Date of Patent: **Apr. 30, 1996**

## [54] LITHIUM BATTERY ELECTRODE COMPOSITIONS

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[21] Appl. No.: **324,371**

[22] Filed: **Oct. 17, 1994**

4,465,743	8/1984	Skarstad et al.	429/105
4,486,400	12/1984	Riley	423/592
4,830,939	5/1989	Leo et al.	429/192
4,932,467	8/1990	Buchel et al.	429/218
4,965,150	10/1990	Dahn et al.	429/218
5,013,620	5/1991	Mlynzaki et al.	429/194
5,039,582	8/1991	Pistoin	429/218
5,336,572	8/1994	Koksbang	429/218
5,340,671	8/1994	Koksbang	429/218

## Related U.S. Application Data

[63] Continuation of Ser. No. 40,224, Mar. 30, 1993, abandoned.

[51] Int. Cl.<sup>8</sup> ..... H01B 1/00; H01B 1/04;  
H01B 1/08; H01M 4/58

[52] U.S. Cl. .... 252/506; 252/502; 252/518;  
429/209; 429/212; 429/218; 429/232

[58] Field of Search ..... 252/502, 506,  
252/518; 429/209, 212, 218, 232

## [56] References Cited

### U.S. PATENT DOCUMENTS

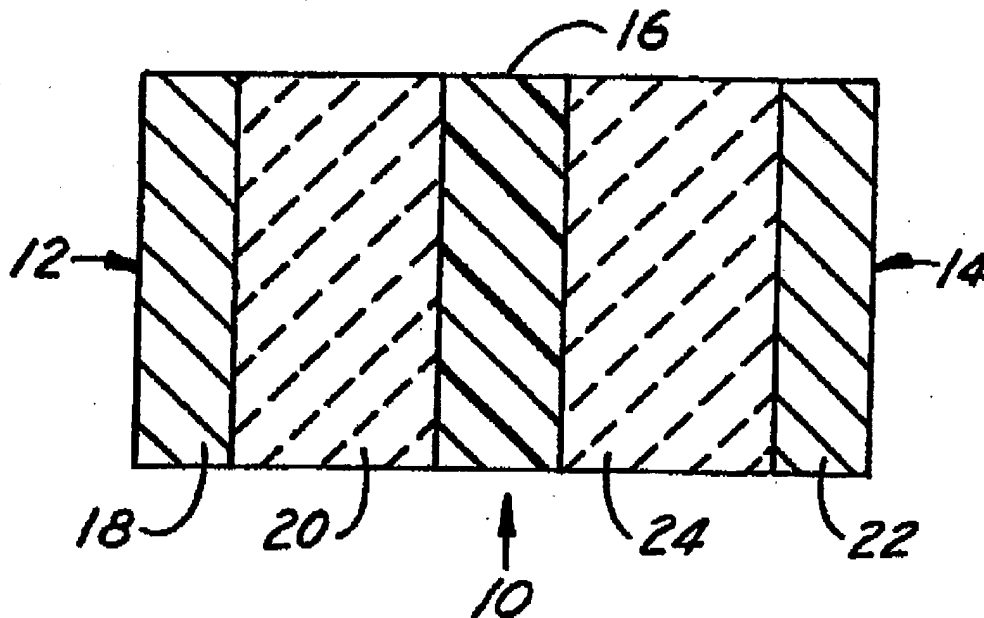
4,144,384	3/1979	Jacobson et al.	429/218
4,243,624	1/1981	Jacobson et al.	264/82
4,310,609	1/1982	Liang et al.	429/218

Primary Examiner—Paul Lieberman  
Assistant Examiner—M. Kopce

## [57] ABSTRACT

A process of making lithium battery electrode active material having fine particles of vanadium oxide ( $V_2O_5$ ) or lithium-vanadium oxide ( $Li_xV_2O_5$ ) intimately mixed with fine particles of carbon. The process includes forming a wet solution of a vanadium oxide precursor and carbon, and then decomposing the precursor/carbon mixture at an elevated temperature or by atomization in a controlled atmosphere. Alternatively, fine particles of vanadium oxide are formed from precursor halogen compounds by atomization in oxygen.

22 Claims, 1 Drawing Sheet





U.S. Patent

Apr. 30, 1996

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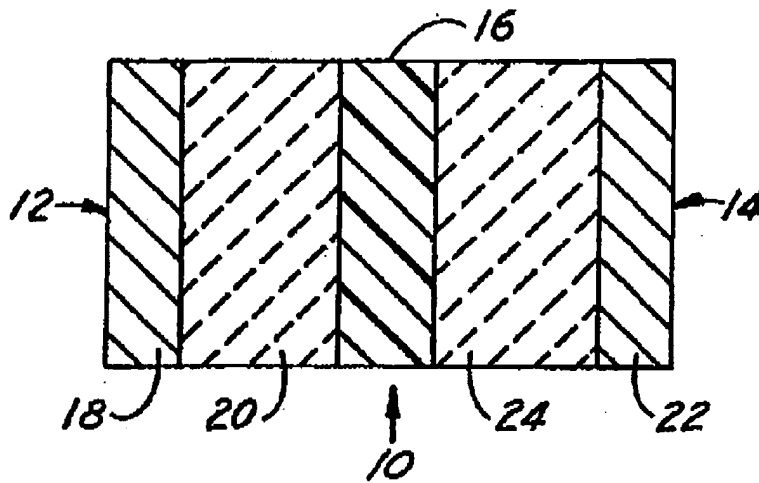


Fig. 1

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**LITHIUM BATTERY ELECTRODE COMPOSITIONS**

This is a continuation of application Ser. No. 08/040,224 filed on Mar. 30, 1993 now abn.

**FIELD OF THE INVENTION**

This invention relates to electrochemical batteries and more particularly to improved positive electrode material for use with lithium-containing negative electrodes.

**BACKGROUND OF THE INVENTION**

The electronic conductivity of transition metal oxides, is generally lower than the electronic conductivity of transition metal sulphides. It is possible to make battery cathodes containing transition metal sulphide active material and a binder. However, it is necessary to add carbon to the composite cathode when the active material is based on an oxide. The requirement for carbon and the amount thereof depends, to some extent, on the specific oxide. The electronic conductivity of vanadium oxides decreases substantially (2-4 orders of magnitude) during lithium insertion, upon discharge of a battery. This increases the need for even greater amounts of added carbon. The amount of carbon added is usually equivalent to about 40-50% by volume of the cathode mixture. This depends on the relative densities of the carbon and the other components in the cathode. Methods which allow reduction of the carbon content are important in order to increase the specific energies of the battery.

Current batteries contain high surface area oxide powders obtained by milling of precursor material. Current methods for the manufacture of powders involve mechanical grinding of precursor material prepared, for example, by rapid quench of molten material or by precipitation from an aqueous solution. As a result, the precursor material is in the form of lumps or large particles. By standard milling techniques it is difficult to reduce the lumps to less than 100 micrometers and very difficult to grind them to less than 10 to 50 micrometers. Smaller particle sizes are desirable because the larger the surface area, the higher is the current drawn from a battery while the current density on the surface of the active material remains low which allows high utilization of the active material.

**SUMMARY OF THE INVENTION**

According to one aspect of the invention, there is provided a method for preparing an electrode material comprising an oxide of vanadium (vanadium oxide) and carbon, in which a solution or wet mixture comprising a compound containing vanadium oxide is prepared with fine particles of carbon dispersed therein. The solution is then dried while maintaining dispersion of the carbon particles, and then is heated for a time and at a temperature sufficient to decompose the vanadium oxide (precursor) to one or more oxides of vanadium, but insufficient to ignite the fine particles of carbon. Carbon particles are formed from precursor materials (i.e. acetylene) at temperatures of about 800° C. Thus, a suitable upper limit for the process of the invention is 800° C. However, lesser temperatures, as low as about 300° C., may be used. The decomposition may occur in minutes, depending on the temperature used. The product so formed has vanadium oxide particles intermingled with fine particles of carbon.

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Suitable precursors of the vanadium oxides are compounds selected from the group consisting of  $\text{NH}_4\text{VO}_3$ , and vanadium oxide halogen compounds such as  $\text{VOF}_2$ ,  $\text{VOBr}$ ,  $\text{VOBr}_2$ ,  $\text{VOBr}_3$ ,  $\text{VOCl}$ ,  $\text{VOCl}_2$ ,  $\text{VOCl}_3$ , and similar compounds having the Br and Cl replaced by I or F. In the case of  $\text{NH}_4\text{VO}_3$ , the wet mixture is desirably aqueous; and the  $\text{NH}_4\text{VO}_3$  (ammonium metavanadate) is the precursor of the  $\text{V}_2\text{O}_5$  (vanadium pentoxide). The  $\text{V}_2\text{O}_5$  intermingled with carbon is formed by preparing an aqueous solution comprising ammonium metavanadate and fine particles of carbon dispersed in the aqueous solution. The aqueous solution is dried while maintaining dispersion of the carbon particles and then the ammonium metavanadate is decomposed to form  $\text{V}_2\text{O}_5$  intermingled with the carbon particles.

In a series of additional steps, the  $\text{V}_2\text{O}_5$  intermingled with the fine carbon particles may be included in a second wet mixture comprising  $\text{LiOH}$ . A reaction is conducted so as to form  $\text{LiV}_3\text{O}_8$  intermingled with the particles of carbon.

In the case of  $\text{VOF}_2$ ,  $\text{VOBr}$ ,  $\text{VOBr}_2$ ,  $\text{VOCl}$ , the wet mixture is desirably non-aqueous. Vanadium oxide halogens such as  $\text{VOCl}_2$ ,  $\text{VOCl}_3$  and  $\text{VOBr}$  are liquid or very deliquescent and may be mixed with carbon with or without a non-aqueous solvent.

The decomposition of the vanadium oxide compound occurs in a range of about 200° C. to about 500° C. with various compounds having various decomposition temperatures. When decomposition is conducted in an environment which is essentially oxygen-free, the oxide of vanadium so formed is represented by the nominal formula  $\text{V}_2\text{O}_5$ . When the decomposition is performed in an oxygen-containing environment, the oxide of vanadium produced is represented by the nominal formula  $\text{V}_2\text{O}_5$ .

When decomposition occurs in an oxygen-containing environment, so as to cause formation of  $\text{V}_2\text{O}_5$ , additional steps can be added in order to form a lithium/vanadium oxide of the nominal formula  $\text{LiV}_3\text{O}_8$  intermingled with the fine carbon particles, similar to the steps described with respect to the  $\text{NH}_4\text{VO}_3$  precursor. The additional steps include forming a second wet mixture comprising  $\text{V}_2\text{O}_5$  and lithium hydroxide and reacting the lithium hydroxide with the  $\text{V}_2\text{O}_5$  to provide the  $\text{LiV}_3\text{O}_8$  intermingled with fine particles of carbon.

Preferably, the reaction takes place at a temperature of at least about 20° C. It occurs more rapidly in a range of about 20° C. to about 60° C. It is desired that the  $\text{LiOH}$  be present in an amount sufficient to provide at least one mole of Li for each 1.5 moles of the  $\text{V}_2\text{O}_5$ .

In still another embodiment, fine particles of an oxide of vanadium are prepared by decomposition of a precursor by spray drying or atomizing. In this method, a liquid containing a vanadium oxide compound is atomized by contacting the liquid with a humidified gas stream at a temperature greater than the temperature of the liquid thereby providing very fine particles of an oxide of vanadium. Suitable vanadium oxides include vanadium oxide halogen compounds. Vanadium oxide halogen compounds which are suitable include:  $\text{VOCl}$ ,  $\text{VOCl}_2$ ,  $\text{VOCl}_3$ ,  $\text{VOBr}$ ,  $\text{VOBr}_2$ ,  $\text{VOBr}_3$  and  $\text{VOF}_2$ . These compounds are readily decomposed in humidified air to form vanadium oxides  $\text{V}_2\text{O}_5$ . Similar vanadium oxide halogen compounds having the Br, or Cl, replaced by I, or F, (x=1, 2 or 3) may also be used. Among these vanadium compounds,  $\text{VOCl}_2$ ,  $\text{VOCl}_3$  and  $\text{VOBr}_3$  are in a liquid or very deliquescent state and optionally include a solvent. In the case of the others, the liquid to be atomized includes a carrier solvent, preferably a non-aqueous, organic solvent.

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If desired, prior to atomization, the liquid containing the vanadium oxide compound may also include fine particles of carbon which are ejected into the atomized stream along with the vanadium oxide compound. This forms fine particles of vanadium oxide  $V_2O_5$  intermingled with carbon particles.

It is an object of the invention to provide electrodes of improved specific energies by reducing vanadium oxide particle size and by improving contact between oxide particles and conductive carbon of the electrode. Other objects include reducing cost of production, reducing or eliminating milling, and increasing consistency and purity of the electrode active material.

These and other objects, features and advantages will become apparent from the following detailed description of the preferred embodiments, appended claims and accompanying drawings.

### BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is an illustration of a cross-section of a thin battery or cell embodying the invention.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As shown in the drawing, a lithium electrochemical cell or battery 10 has a negative electrode side 12, a positive electrode side 14, and a separator 16 therebetween. In accordance with common usage, a battery may consist of one cell or multiple cells. The negative electrode is the anode during discharge, and the positive electrode is the cathode during discharge. The negative electrode side includes current collector 18, typically of nickel, iron, stainless steel, and/or copper foil, and a body of negative electrode active material 20. The negative electrode active material 20 is sometimes simply referred to as the negative electrode. The positive electrode side includes current collector 22, typically of aluminum, nickel, iron, stainless steel, and/or copper foil (such foils usually have a protective conducting coating), and a body of positive electrode active material 24 which has as its main component one or more oxides of vanadium. The positive electrode active material 24 is sometimes simply referred to as the positive electrode. The separator 16 is typically a solid electrolyte, or electrolyte separator. A suitable electrolyte separator (polymer electrolyte) is described in U.S. Pat. No. 4,830,939, incorporated herein by reference. The electrolyte separator is a solid organic polymer matrix containing an ionically conducting liquid with an alkali metal salt and the liquid is an aprotic polar solvent.

In one embodiment, positive electrode active material of vanadium oxide is intermingled with carbon and is prepared from an ammonium metavanadate precursor. The ammonium metavanadate ( $NH_4VO_3$ ) may be prepared from alkali solutions of  $V_2O_5$  and precipitation with ammonium chloride. The starting material, ammonium metavanadate, is dissolved in solution, preferably an aqueous solution. Ammonium metavanadate is soluble in 165 parts water, and its solubility increases with temperature. Ammonia enhances solubility in water.

Next, a desired amount of carbon is dispersed in the aqueous solution. The solution is dried and in the preferred method, water is removed by evaporation while the carbon is dispersed in the solution by stirring or by agitation of the reaction vessel.

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The final step of the process consists of heating the dried mixture of carbon and ammonium metavanadate for a time and at a temperature sufficient to decompose the ammonium metavanadate to one or more oxides of vanadium, but at a temperature insufficient to ignite the fine particles of carbon. When the decomposition is conducted in an oxygen-containing environment, the vanadium oxide, produced by such decomposition, has the nominal formula  $V_2O_5$  (vanadium pentoxide). When the decomposition step is conducted in an essentially oxygen-free environment, the vanadium oxide so produced is represented by the nominal formula  $V_6O_{13}$ . Preferably, the non-oxygen containing environment is an inert gas stream, such as argon or nitrogen, whereby the  $NH_4VO_3$  is decomposed to  $V_6O_{13}$ . Thus,  $V_2O_5$  and  $V_6O_{13}$  are each formed from the decomposition product of  $NH_4VO_3$  while being intermingled with carbon particles. The product is thus essentially in the form of carbon particles coated with the vanadium oxide or, depending on the relative sizes of the carbon particles and the vanadium oxide particles, the oxide particles may be coated with carbon. In any event, intimate mixing and intimate contact between carbon grains and oxide grains is achieved.

It is thought that the step of heating to decompose may be conducted at a temperature in the range of 400° C. to 450° C. or somewhat less because the carbon may act as a catalyst for the decomposition reaction. Thus, a temperature as low as about 300° C. may be selected. An advantage of the method is that the intimately mixed carbon and vanadium oxide is formed by heating in an atmosphere which contains  $NH_3$  formed by decomposition of the ammonium metavanadate. This is thought to be beneficial because the reducing effect of  $NH_3$  at 400° C. may remove sulfur and organic impurities present in the carbon particles. Suitable carbon particles are Ketjen Black or Shawinigan Black which are mixed with the starting  $NH_4VO_3$  prior to evaporation of the solvent and decomposition of the  $NH_4VO_3$ , as stated above. Carbon particles are formed from precursor materials (i.e. acetylene) at temperatures of about 800° C. Thus, a suitable upper limit for the process of the invention is 800° C. However, lesser temperatures, as low as about 300° C., may be used. The decomposition may occur in minutes, depending on the temperature used.

Preferably, the carbon particles are impregnated with an aqueous solution of the  $NH_4VO_3$ . Preferably, after dispersion of the carbon in the  $NH_4VO_3$  solution, the excess solvent is removed by evaporation, filtering and/or vacuum drying. Elevated temperature may be used to speed the drying process.

Carbon particles may be obtained from Noury Chemical Corporation, under the designation Ketjen Black. The Ketjen Black particles, in an as-received condition, have a BET surface area of approximately 900 m<sup>2</sup>/gram. Ketjen Black has an average particle size or equivalent average diameter in the range of about 10 to 100 nanometers (0.01 to 0.1 microns), and typically in the order of 30 nanometers. Thus, the carbon particles and oxide particles are very fine and of micron or submicron size.

The advantages of this procedure are that there is improved grain-to-grain contact between carbon and vanadium oxide particles ( $V_2O_5$  or  $V_6O_{13}$ ), and also between the various carbon particles, which enhances the electric contacts in the carbon and vanadium oxide network of the composite electrode. Another advantage is that the decomposition may occur in a temperature of about 300° C. or less, as compared to the 400° C. for decomposition of  $NH_4VO_3$  in the absence of carbon. Thus, the process of the invention reduces energy requirements and preparation costs. Still,

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another advantage is that vanadium oxide particles are formed having an average size less than 100 microns, desirably less than 50 microns and, preferably, less than 10 microns. It should be noted that median particle size refers to that size at which 50% by weight of the particles are, respectively, above and below in size.

In another embodiment, the method of the invention can be used to prepare  $\text{LiV}_3\text{O}_8$  in a completely amorphous state and in intimate contact with particles of carbon. The amorphous state is beneficial for rate capabilities and energy density. This composite is prepared by forming a  $\text{V}_2\text{O}_5$ /carbon mixture, as described above. This  $\text{V}_2\text{O}_5$ /carbon composition is then dispersed in a solution of  $\text{LiOH}$  in water, where the amount of  $\text{V}_2\text{O}_5$  and  $\text{LiOH}$  corresponds to the stoichiometric amounts of the two compounds needed for formation of  $\text{LiV}_3\text{O}_8$ . It is thought that part of the  $\text{V}_2\text{O}_5$  dissolves in solution, followed by reaction between the dissolved  $\text{V}_2\text{O}_5$ ,  $\text{LiOH}$  and water and then with the remaining solid  $\text{V}_2\text{O}_5$ , with the subsequent formation of  $\text{LiV}_3\text{O}_8$ . The reaction is fairly slow at room temperature, but proceeds at a reasonable rate at a  $50^\circ\text{C}$ . to  $60^\circ\text{C}$ . A process of adding progressive amounts of vanadium pentoxide to an  $\text{LiOH}$  solution is more fully described in U.S. Pat. No. 5,039,582, which is incorporated herein in its entirety by reference. The reaction to form  $\text{LiV}_3\text{O}_8$  is conducted while keeping the carbon and undissolved  $\text{V}_2\text{O}_5$  dispersed in solution, so that the contact between the product  $\text{LiV}_3\text{O}_8$  and the carbon is optimized. Advantageously, because part of the  $\text{V}_2\text{O}_5$  is dissolved during the procedure, intimate mixing between the  $\text{V}_2\text{O}_5$  precursor from which the  $\text{LiV}_3\text{O}_8$  is formed and the carbon, is essentially automatically achieved. Particle size of the lithium vanadium oxide is on the order of that described earlier in connection with  $\text{V}_2\text{O}_5$  and  $\text{V}_6\text{O}_{13}$ .

In still another embodiment, other vanadium oxide compounds are decomposed to form binary vanadium oxides  $\text{V}_x\text{O}_y$  intermingled with fine carbon particles. Suitable vanadium oxide compounds include vanadium oxide halogens such as  $\text{VOBr}_2$ ,  $\text{VOBr}_3$ ,  $\text{VOCl}$  and  $\text{VOF}_2$  which are all thought to decompose below  $200^\circ\text{C}$ . except  $\text{VOBr}$  which decomposes at a temperature of about  $480^\circ\text{C}$ . Others are  $\text{VOCl}_2$ ,  $\text{VOCl}_3$  and  $\text{VOBr}_2$  which are liquids and, therefore, easy to mix with carbon or absorb carbon. The family of vanadium oxide halogens which are useful in the process are represented by the general formula  $\text{V}_x\text{O}_y\text{M}_z$  where  $x=1, 2$  or  $3$ .

In the basic method, the vanadium oxide halogen compound is mixed with particles of carbon, forming a wet mixture. The solvent is then dried while maintaining dispersion of the carbon particles, and then is heated for a time and at a temperature sufficient to decompose the vanadium oxide compound to one or more oxides of vanadium, but insufficient to ignite the fine particles of carbon. The product so formed comprises particles of one or more oxides of vanadium intermingled with fine particles of carbon. Given the presence of carbon, which acts as a catalyst, reduction of the stated decomposition temperatures is possible. It should be noted that at lower decomposition temperatures, some compounds may become less stable and may react with water and, therefore, require handling under inert gas conditions, or with a non-aqueous solvent.

In still another embodiment, finely dispersed powders of binary vanadium oxides are formed from vanadium oxide halogens ( $\text{V}_x\text{O}_y\text{M}_z$ ,  $\text{M}=\text{Cl}, \text{Br}, \text{F}$  or  $\text{I}$ ) by decomposition in a moist atmosphere by atomization. Such compounds are exemplified by the general formula  $\text{V}_x\text{O}_y\text{M}_z$  where  $x=1, 2$  or  $3$ . Among the vanadium oxide halogen compounds,  $\text{VOCl}_2$ ,  $\text{VOCl}_3$  and  $\text{VOBr}_2$  are particularly suitable because they are liquids and a carrier solvent (dispersant) may not be required for atomization or spray drying. Other vanadium oxide halogen compounds such as  $\text{VOBr}$ ,  $\text{VOBr}_2$ ,  $\text{VOCl}$  and

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$\text{VOF}_2$ , are not typically in a liquid condition, these compounds may be dissolved or dispersed in a non-aqueous solvent and then atomized to achieve finely dispersed binary  $\text{V}_x\text{O}_y$  powders. When the decomposition takes place in open air, the major component of such decomposition will be  $\text{V}_2\text{O}_5$ . However, by adjusting the reducing properties of the atmosphere, various vanadium oxides in the form of fine particles may be obtained. Such particles are of micron or submicron size. In the absence of carbon the finely dispersed vanadium oxide powders so produced are then mixed with carbon without the necessity of ball-milling to achieve intimate contact. Alternatively, fine particles of carbon may be included in the liquid prior to atomizing. The conditions for atomization are rather broad and include forming droplets in a gas stream containing water, i.e. humidified gas stream. The conditions for decomposition of an atomized stream of VO halogen compounds ( $\text{V}_x\text{O}_y\text{M}_z$ ) are rather broad. From a practical view point, there must be sufficient humidity to permit reaction between  $\text{V}_x\text{O}_y\text{M}_z$  molecules and droplets or molecules of water. Thus, even a small amount of water in an air stream will yield some binary oxide product. As the air is made more humid, the dispersion and diffusion of water molecules result in improved contact with  $\text{V}_x\text{O}_y\text{M}_z$  molecules, and a greater yield of binary  $\text{V}_x\text{O}_y$  product. The temperature of such process must be sufficient to prevent recondensation of water and consequential reduction of water in the humid air. It is possible to conduct the atomization/decomposition at about room temperature, i.e. about  $10^\circ\text{C}$ . to about  $40^\circ\text{C}$ ., and then adjust the flow of atomized  $\text{V}_x\text{O}_y\text{M}_z$  and humid air to achieve a desired yield. The theoretical upper temperature limit is that at which decomposition of the desired binary oxide product, or carbon particles intermingled therewith, occurs. This is thought to be on the order of about  $800^\circ\text{C}$ .

The vanadium oxides of the invention were used to prepare cells with lithium-based anodes. Several cells were prepared by mixing oxide active material carbon (typical Shawinigan Black) and electrolyte/binder. The oxides were prepared with and without carbon. Thus, in some cases, carbon particles were added after fine particles of the oxide had been formed. A typical composition is as given in Table 1.

TABLE 1

Typical Cathode Composition	Percent by Weight
Vanadium Oxide	45.2%
Carbon	10.3%
Propylene Carbonate (PC)	33.3%
Polyethylene Oxide (PEO)	1.0%
PolyEthylene GlycolDiAcrylate (PEODA)	8.8%
TriMethylPolyEthylene Oxide TriAcrylate (TMPEOTA)	1.5%

The cathode was coated onto nickel foil followed by electron beam curing (cross-linking/polymerization) of the acrylate component. Then the electrolyte was coated on top of the cathode and cured with ultraviolet light. The lithium electrode was applied on top of the electrolyte separator and the battery was finally placed in a flexible pouch which was heat sealed under vacuum.

The energy density of the batteries based on these new electrode materials is improved. That is believed to be achieved by decreasing the carbon content of the cathode, providing better contact between the carbon and the vanadium oxide, and keeping the carbon content at a lesser level than would otherwise be required due to the increased contact which increases the electronic conductivity allowing higher current drains, while the energy density remains essentially unchanged. Particle size is on the order of less than 100 microns, desirably less than 50 microns and, preferably, less than 10 microns.

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The method of the invention eliminates, or at least reduces, the need for standard milling techniques, whereby it is difficult to reduce particle size to less than about 100 microns. Since suitable particle size, less than 50 microns and, preferably, less than 10 microns is achieved by intimate mixing with carbon to form an electronically conducting carbon network with good contact to the active material on a microscopic scale, the invention avoids heavy-duty milling methods. However, if desired, milling of the final product is possible and desired for mixing of carbon with oxide particles if such carbon was not previously included. The degree of any milling is greatly reduced. That is, the mixing force of any subsequent milling step would be very much be reduced.

While this invention has been described in terms of certain embodiments thereof, it is not intended that it be limited to the above description, but rather only to the extent set forth in the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined in the appended claims.

1 claim:

1. A method of preparing a composition for an electrode comprising forming a wet mixture consisting essentially of ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) and fine particles of carbon dispersed in a solvent, removing at least a portion of the solvent and decomposing the ammonium metavanadate in an oxygen-containing environment at a temperature sufficient to form particles of an oxide of vanadium represented by the nominal general formula  $\text{V}_2\text{O}_5$  intermingled with and in grain-to-grain contact with the fine carbon particles.

2. The method according to claim 1, wherein the decomposition temperature is in a range of about  $300^\circ\text{C}$ . to about  $450^\circ\text{C}$ .

3. The method according to claim 1, wherein said at least portion of the solvent is removed from the mixture by filtration or vacuum sensation.

4. The method according to claim 1, wherein said at least a portion of the solvent is removed by heating to a temperature less than the decomposition temperature.

5. The method according to claim 1 and further comprising after said decomposition;

forming a second wet mixture comprising the decomposition product and lithium hydroxide ( $\text{LiOH}$ ), and reacting the  $\text{LiOH}$  with the decomposition product for a time and at a second temperature sufficient to provide lithium-vanadium oxide of the nominal formula  $\text{LiV}_2\text{O}_6$  intermingled with and in grain-to-grain contact with the fine carbon particles.

6. The method according to claim 5, wherein the second temperature is at least about  $20^\circ\text{C}$ .

7. The method according to claim 5, wherein the second temperature is in a range of about  $20^\circ\text{C}$ . to about  $60^\circ\text{C}$ .

8. The method according to claim 5, wherein the  $\text{LiOH}$  is present in an amount sufficient to provide at least one mole of  $\text{Li}$  for each 1.5 moles of the  $\text{V}_2\text{O}_5$ .

9. A method of preparing a composition for an electrode, comprising:

a) forming a mixture comprising a vanadium oxide halogen compound and fine particles of carbon dispersed in the mixture; and

b) decomposing the vanadium oxide halogen compound to form particles of one or more oxides of vanadium, and intermingling the particles of the one or more oxides of vanadium with the fine carbon particles in grain-to-grain contact therewith.

10. The method according to claim 9, wherein the mixture of step (a) includes a solvent and before step (b) at least a portion of the solvent is removed from the mixture.

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11. The method according to claim 9, wherein the vanadium oxide halogen compound is selected from the group consisting of  $\text{VOF}_2$ ,  $\text{VOBr}$ ,  $\text{VOBr}_2$ ,  $\text{VOBr}_3$ ,  $\text{VOCl}$ ,  $\text{VOCl}_2$ , and  $\text{VOCl}_3$ .

12. The method according to claim 9, wherein the temperature is in a range of about  $200^\circ\text{C}$ . to about  $500^\circ\text{C}$ .

13. The method according to claim 9, wherein step (b) is conducted in an environment which is essentially oxygen-free, thereby providing the oxide of vanadium represented by the nominal formula  $\text{V}_2\text{O}_5$ .

14. The method according to claim 9, wherein step (b) is conducted in an oxygen-containing environment thereby providing the oxide of vanadium represented by the nominal formula  $\text{V}_2\text{O}_5$ .

15. The method according to claim 14 and further comprising;

forming a second mixture comprising the product of step (b) and lithium hydroxide ( $\text{LiOH}$ ), and reacting such mixture of  $\text{LiOH}$  and said product of step (c) for a time and at a second temperature sufficient to provide lithium-vanadium oxide of the nominal formula  $\text{LiV}_2\text{O}_6$  intermingled with the fine carbon particles.

16. The method according to claim 15, wherein the second temperature is at least about  $20^\circ\text{C}$ .

17. The method according to claim 15, wherein the second temperature is in a range of about  $20^\circ\text{C}$ . to about  $60^\circ\text{C}$ .

18. The method according to claim 15, wherein the  $\text{LiOH}$  is present in an amount sufficient to provide at least one mole of  $\text{Li}$  for each 1.5 moles of the  $\text{V}_2\text{O}_5$ .

19. The method according to claim 1 wherein the solvent removal and the decomposition are each conducted at an elevated temperature, and the solvent removal temperature is less than the decomposition temperature.

20. The method according to claim 9 wherein the mixture of step (a) includes a solvent, before step (b) at least a portion of the solvent is removed from the mixture, the solvent removal and the decomposition are each conducted at an elevated temperature, and the solvent removal temperature is less than the decomposition temperature.

21. A method of preparing a composition for an electrode, comprising:

a) forming a mixture consisting essentially of ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) and fine particles of carbon dispersed in a solvent;

b) drying the mixture at a first temperature while maintaining dispersion of the carbon particles; and

c) heating the product of step (b) for a time and at a second temperature greater than the first temperature and sufficient to decompose the ammonium metavanadate in an oxygen-containing environment to form particles of one or more oxides of vanadium and insufficient to ignite the fine particles of carbon, and intermingling the particles of the one or more oxides of vanadium with the fine carbon particles in grain-to-grain contact therewith.

22. The method according to claim 21 and further comprising after step (c);

forming a second wet mixture comprising the product of step (c) and lithium hydroxide ( $\text{LiOH}$ ), and reacting the  $\text{LiOH}$  with the product of step (c) for a time and at a third temperature less than the second temperature and sufficient to provide lithium-vanadium oxide of the nominal formula  $\text{LiV}_2\text{O}_6$  intermingled with and in grain-to-grain contact with the fine carbon particles.

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## United States Patent [19]

Takamuki et al.

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[45] Date of Patent: Sep. 17, 1996

[54] SILVER HALIDE PHOTOGRAPHIC  
ELEMENT AND PROCESSING METHOD  
THEREOF

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[56] References Cited

## U.S. PATENT DOCUMENTS

1,574,944 3/1926 Sheppard .  
1,602,592 10/1926 Sheppard .  
1,623,499 4/1927 Sheppard et al. .  
2,193,015 3/1940 Weissberger ..... 95/88  
2,278,668 4/1942 Piety ..... 172/245  
2,278,947 4/1942 Reister ..... 95/7  
2,410,689 11/1946 Sheppard ..... 95/7  
2,592,364 4/1952 Weissberger et al. .... 95/88  
2,701,245 2/1955 Lynn ..... 260/89.5  
2,992,101 7/1961 Jelley et al. .... 96/23  
3,297,446 1/1967 Dunn ..... 96/107  
3,297,447 1/1967 McVeigh ..... 96/109  
3,320,069 5/1967 Illingsworth ..... 96/107  
3,408,196 10/1968 McVeigh ..... 96/108  
3,408,197 10/1968 McVeigh ..... 96/108

3,420,670 1/1969 Miltoo ..... 96/109  
3,442,653 5/1969 Dunn ..... 96/108  
3,489,576 1/1970 Vincent et al. .... 106/1  
3,501,313 3/1970 Willemis et al. .... 96/107  
3,531,289 9/1970 Wood ..... 96/108  
3,591,385 7/1971 Evans ..... 96/107  
3,655,394 4/1972 Illingsworth ..... 96/108  
3,656,955 4/1972 Ushimaru et al. .... 96/107  
3,772,031 11/1973 Berry et al. .... 96/108  
4,047,958 9/1977 Yoneyama et al. .... 96/87 R  
4,126,459 11/1978 Greenwald ..... 96/29  
4,142,894 3/1979 Hori et al. .... 96/63  
4,396,706 8/1983 Ishii et al. .... 430/403  
4,414,304 11/1983 Dickerson ..... 430/353  
4,425,425 1/1984 Abbott et al. .... 430/502  
4,439,520 3/1984 Kofron et al. .... 430/434  
4,711,838 12/1987 Grzeskowiak et al. .... 430/568  
5,098,818 3/1992 Ito et al. .... 430/536

## FOREIGN PATENT DOCUMENTS

0556845 8/1993 European Pat. Off. .  
6-95300 4/1994 Japan .

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Garrett & Dunner, L.L.P.

## [57] ABSTRACT

A silver halide photographic element with enhanced sensitivity and improved pressure resistance is disclosed, comprising a support having, on at least one side thereof, hydrophilic colloidal layers including a light-sensitive silver halide emulsion layer and a nonlight-sensitive hydrophilic colloidal layer, wherein the nonlight-sensitive layer contains organic material-aggregation particles; and gelatin contained in the total hydrophilic colloidal layers provided on one side of the support amounts to a range of 1.3 to 2.5 g per m<sup>2</sup>.

10 Claims, No Drawings

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# SILVER HALIDE PHOTOGRAPHIC ELEMENT AND PROCESSING METHOD THEREOF

## FIELD OF THE INVENTION

The present invention relates to a silver halide photographic element and a processing method thereof, and particularly to a silver halide photographic element high in sensitivity and excellent in pressure characteristics even when the total processing time is 30 seconds or less at a reduced developer-replenishing rate.

## BACKGROUND OF THE INVENTION

Recently, a rapid advancement in shortening of access time to an image has been made through progress in electronics, leading to further demand for more rapid processing of a silver halide element.

Technique have been known for promoting photographic-processing speed such as a developing rate, fixing rate, washing rate or drying rate by reducing the amount of gelatin used as a binder for dispersing and protecting silver halide grains to provide rapid-processability.

With reduction of the amount of gelatin used, highly sensitive silver halide grains become increasingly less able to resist external pressure, so that, when processed in an automatic processor, numerous small spot-like uneven density, so-called roller marks, produced by pressure due to unevenness of the transporting rollers operating in the developing bath of the automatic processor. Especially when processed within a total processing time of 30 seconds, the roller mark problem becomes pronounced.

Recently, furthermore, environmental pollution has been viewed as a world-wide problem, causing a rise in interest in waste-material at home and abroad to the point that responsibility for reduction in waste-material at the corporate level has been called for.

Under these conditions, reduction of photographic processing effluent becomes an urgent problem to be solved. In order to achieve such reductions, there were disclosed techniques of making tabular silver halide grains or applying selenium-sensitization to silver halide grains, as shown, for example, in JP-A 4-291252/1992 (the term "JP-A" herein means an "unexamined published Japanese patent application"). However, the level of reduction in the replenishing rate is still insufficient and it was found that further reduction lowered the level to pressure resistance.

## SUMMARY OF THE INVENTION

An object of the present invention is to provide a photographic element high in sensitivity, improved in pressure resistance and suited for rapid-processing without causing the roller marks to occur even when processed at a low replenishing rate in view of environment, and a processing method thereof.

The object of the invention can be accomplished by a silver halide photographic element comprising a support having thereon a silver halide emulsion layer and a nonlight-sensitive hydrophilic colloid layer, wherein said nonlight-sensitive hydrophilic colloid layer contains organic material-aggregating particles and the total amount of gelatin contained in all hydrophilic colloid layers provided on one side of the support is 1.3 to 2.5 g per m<sup>2</sup>.

## DETAIL DESCRIPTION OF THE INVENTION

The organic material-aggregation particles used in the invention are each comprised of fine particles of organic material in an aggregated form. Thus, a plurality of fine particles of an organic material (primary particles) having an average size of 0.05 to 0.50  $\mu\text{m}$ , aggregate with each other to form particles having an average size of 1.0 to 20.0  $\mu\text{m}$ .

The aggregation particles may be either spherical or in an unfixed form. The organic material comprises a homopolymer of alkyl methacrylate, alkyl acrylate, fluorine- or silicon-substituted alkyl methacrylate, acrylate or styrene, or a copolymer thereof. As examples of monomer components, are cited methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, methyl methacrylate, ethyl acrylate, n-butyl acrylate, 2-hydroxyethyl methacrylate, 2-methoxyethyl methacrylate, 2-methanesulfonamidoethyl methacrylate, trifluoromethyl methacrylate-trihydroxysilylpropyl methacrylate. Examples of polymers are as follows, in which the weight ratio of monomers is shown in the parentheses. Aggregation particles thereof are prepared so as to have an average size of 4.0  $\mu\text{m}$ , comprising primary particles having an average size of 0.1  $\mu\text{m}$ .

B-1	Polymethyl methacrylate
B-2	Polystyrene
B-3	(Methyl methacrylate/ethyl methacrylate) copolymer (90/10)
B-4	(Methyl methacrylate/ethyl methacrylate) copolymer (50/50)
B-5	(Methyl methacrylate/ethyl methacrylate) copolymer (20/80)
B-6	(Methyl methacrylate/styrene) copolymer (70/30)
B-7	(Styrene/ethyl methacrylate) copolymer (60/40)
B-8	Polystyrene
B-9	(Trifluoromethyl methacrylate/methyl methacrylate) copolymer (50/50)
B-10	(Trifluoromethyl methacrylate/styrene) copolymer (30/70)
B-11	Polystyrene

Among the above, polymethyl methacrylate is preferable.

As examples thereof are cited GR-5 and GR-5P (product of Sohken Chemicals Corp.). To display effects without causing deterioration in haze, an addition amount thereof is preferably 10 to 200 mg/m<sup>2</sup>. It may be added to any layer such as an emulsion layer or protective layer preferably to a protective layer. Particularly, when the protective layer is divided into two or more layers, it is more preferable to add into an uppermost layer.

In the invention, the amount of gelatin contained in all of hydrophilic colloid layers including an emulsion layer provided on one side of a support is preferably 1.3 to 2.5 g/m<sup>2</sup>, more preferably 1.5 to 2.3 g/m<sup>2</sup>.

As gelatin is cited so-called alkali-treated gelatin or acid-treated gelatin.

As silver halide applicable in the invention, it is preferable to use tabular grains so as to achieve high sensitivity. Any silver halide such as silver bromide, silver chloride, silver chlorobromide, silver iodochlorobromide or silver iodobromide may be optionally usable. Among these, silver iodobromide is preferable.

The tabular grains are described in U.S. Pat. Nos. 4,439,520, 4,425,425 and 4,414,304 and the desired tabular grains can be readily obtained. The tabular grains are able to cause silver halide different in composition to grow epitaxially or shell on a specific site of the surface thereof. Further, to control a sensitivity speck, a dislocation line may be located on the surface or inside of the grain.

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In the invention, tabular grains having an aspect ratio of not less than 2, preferably, account for 50% or more of the projected area of total grains contained in a layer containing the tabular grains.

As the proportion of the tabular grains is increased to 60%, further to 70% and furthermore to 80%, the more preferable results have been achieved. The term, an "aspect ratio" means an ratio of a diameter of a circle equivalent to the projected area of the grain to a distance between two parallel tabular faces. In the invention, the aspect ratio is not less than 2 and less than 20, preferably not less than 3 and less than 16.

Tabular grains of the invention have a thickness of not more than 0.5  $\mu\text{m}$ , preferably not more than 0.3  $\mu\text{m}$ . As to the size distribution of the tabular grains, is preferable a mono-dispersed emulsion having a coefficient of variation of grain size of 30% or less, preferably 20% or less, which is represented by a standard deviation of the grain size (S) divided by an average size (D), i.e.,  $S/D \times 100$  (%). The tabular grains may be mixed with non-tabular regular crystal grains.

To control the grain growth during the course of forming the tabular grains, there may be usable a silver halide solvent such as ammonia, a thioether compound or a thione compound. During the course of physical ripening and chemical ripening, may be addenda a salt of a metal such as zinc, lead, thallium, iridium or rhodium.

In the invention, silver halide grains are preferably chemically-sensitized with a selenium-sensitizer. The selenium sensitizers used for chemical sensitization of the invention include a broad kinds of selenium compounds, as disclosed in U.S. Pat. Nos. 1,574,944, 1,602,592 and 1,623,499, and JP-A 60-150046/1985, 4-25832/1992, 4-109240/1992 and 4-147250/1992. As usable selenium sensitizers, are cited colloidal selenium, isoselenocyanates (e.g., allyl isoselenocyanate), selenourcas (e.g., N,N-dimethylselenourea and N,N,N'-trimethylselenourea, N,N,N'-trimethyl-N'-heptafluoropropylcarbo-nylselenourea and N,N,N'-trimethyl-N'-4-nitrophenylcarbo-nylselenourea), selenoketones (e.g., selenoacetone and selenoacetophenone), selenoamides (e.g., selenoacetamide and N,N-dimethylselenobenzamide), selenocarboxylic acids and selenoesters (e.g., 2-selenopropionic acid and methyl-3-selenobutylate), selenophosphates (e.g., tri-p-triseleno-phosphate) and selenides (diethylselenide, diethyldiselenide and triphenylphosphineselenide). Particularly preferable sensitizers are selenourea, selenoamide and selenoketones. Examples of using techniques of these selenium sensitizers are disclosed in the following patent specifications; U.S. Pat. Nos. 1,574,944, 1,602,592, 1,623,499, 3,297,446, 3,297,447, 3,320,069, 3,408,196, 3,408,197, 3,442,653, 3,420,670 and 3,591,385; French Patent Nos. 2693038 and 2093209; Japanese Patent Nos 52-34491, 52-34492, 53-295 and 57-22090; JP-A 59-180536, 59-185330, 59-181337, 59-181338, 59-192241, 60-150046, 60-151637, 61-246738, 3-4221,3-24537, 3-111838, 3-116132, 3-148648, 3-237450, 4-16838, 4-25832, 4-32831, 4-96059, 4-109240, 4-140738, 4-140739, 4-147250, 4-149437, 4-184331, 4-190225, 4-191729 and 4-195035; British Patent Nos 255846 and 861984; and also in a reference of H. E. Spencer et al., *Journal of Photographic Science* Vol. 31, pages 158-169 (1983).

The using amount of the selenium sensitizer, depending on a selenium compound, silver halide grains and the conditions of chemical ripening, is in general  $10^{-8}$  to  $10^{-4}$  mol per mol of silver halide. The selenium sensitizer may be

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added by dissolving in an organic solvent such as water, methanol, ethanol or ethylacetate or in a mixture thereof, or premixing with an aqueous gelatin solution; or added by dispersing in the form of an emulsion of a mixed solution with organic solvent-soluble polymer as disclosed in JP-A 4-140739.

The temperature of chemical ripening by using a selenium sensitizer is preferably within a range of 40° to 90° C., more preferably 45° to 80° C. The pH and pAg are preferably 4 to 9 and 6 to 9.5, respectively.

In the chemical sensitization of the invention, the selenium sensitization may be combined with sulfur sensitization, tellurium sensitization, reduction sensitization or noble metal sensitization.

As a sulfur sensitizer, is usable those as disclosed in U.S. Pat. Nos. 1,574,944, 2,410,689, 2,278,947, 2,728,668, 3,501,313 and 3,656,955, West German Patent Application (OLS) No.1,422,869, and JP-A 56-24937 and 55-45016. Examples thereof include thiourea derivatives such as 1,3-diphenylthiourea, trichethylthiourea and 1-ethyl-3-(2-thiaz-olyl)thiourea; rhodanine derivatives; dithiocarbamic acids, organic polysulfide compounds and elemental sulfur, which is preferably rhombic  $\alpha$ -sulfur.

The tellurium sensitization and a sensitizing method thereof are disclosed in U.S. Pat. Nos. 1,623,499, 3,320,069, 3,772,031, 3,531,289 and 3,655,394; British Patent Nos. 235,211, 1,121,496, 1,295,462 and 1,396,696; Canadian Patent No. 800,696; JP-A 204640 and 4-333043. Examples of useful tellurium sensitizer include tellouroreas (e.g., N,N-dimethyltellourea, tetramethyltellourea, n-carboxy-ethyl-N,N'-dimethyltellourea and N,N'-dimethyl-N'-phe-nyltellourea), phosphine tellurides (e.g., tributylphosphine telluride, tricyclohexylphosphine telluride, triisopropyl-phosphine telluride, butylisopropylphosphine telluride and dibutylphenylphosphine telluride), telluroamides (e.g., tel-luroacetamide and N,N-dimethyltellurobenzamide), tel-luroketones; telluroesters; and isotellurocyanates. Tech-niques of using the tellurium sensitizer are similar to those of the selenium sensitizer.

In the invention, a combined use of reduction sensitiza-tion is preferable. It is preferable to apply the reduction sensitization during the course of forming silver halide grains. The reduction sensitization is applied not only with growing silver halide grains but also at the state of inter-rupting the grain growth, thereafter, reduction-sensitized grains are further grown.

Gold sensitizers used in the invention include chloroauric acid, gold thiosulfate, gold thiocyanate and gold complexes of thioureas, rhodanines and other compounds.

The using amount of a selenium sensitizer, sulfur sensi-tizer, tellurium sensitizer, reduction sensitizer and gold sensitizer is, depending on the kind of silver halide and the sensitizer, and the ripening condition, preferably within a range of  $1 \times 10^{-4}$  to  $1 \times 10^{-8}$  mol per mol of silver halide, more preferably  $1 \times 10^{-5}$  to  $1 \times 10^{-8}$  mol.

In the invention, the selenium sensitizer, sulfur sensitizer, tellurium sensitizer, reduction sensitizer or gold sensitizer may be added in the form of a solution by dissolving in water, an alcohol or another inorganic or organic solvent; or in the form of a dispersion by dispersing in a water-immiscible solvent a medium such as gelatin.

A sensitizing dye can be optionally used in the invention. Preferably, for example, are usable cyanine dyes such as exemplified compounds of S-11 through S-124 represented by formulas (I) to (III) as disclosed in JP-A 1-100533.

The sensitizing dyes may be added in combination thereof, wherein two or more dyes may be added mixedly at



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the same time or separately at different times. The addition amount thereof is 1 to 1000 mg per mol of silver, preferably 5 to 500 mg. Furthermore, it is preferable to add potassium iodide prior to the addition the sensitizing dye.

The sensitizing dye of the invention may be added during the period of forming silver halide grains or at any time after grain-forming and before coating. It is preferable to add the dye prior to the completion of desalting.

At the time when adding the dye, the pH of a reaction solution (conventionally, in a reaction vessel) is preferably within a range of 4 to 10, more preferably 6 to 9. The pAg of the reaction solution is preferably within a range of 5 to 11.

The sensitizing dye of the invention may be dispersed directly in an emulsion. The dye is also dissolved in an optimal solvent methanol, ethanol, methyl cellosolve, acetone, water, pyridine or a mixture thereof to be added in the form of a solution. Ultrasonic may be employed for dissolution thereof. The dye may be added in the form of solid particles dispersed by use of a high-speed impeller.

An inorganic fine particles having a particle size of 1 to 300 nm of the invention is an oxide compound comprising, as main component, silicon, aluminium, titanium, indium, yttrium, tin, antimony, zinc, nickel, copper, iron, cobalt, manganese, molybdenum, niobium, zirconium, vanadium, alkali metal or alkali earth metal. Among these, from the viewpoint of transparency and hardness, is preferable silicon oxide (colloidal silica), aluminum oxide, antimony oxide, titanium oxide, zinc oxide, zirconium oxide, tin oxide, vanadium oxide or yttrium oxide. These inorganic oxide particles may be surface-treated with alumina, yttrium or cerium so as to enhance dispersion stability in water when dispersed in water to form a sol. Examples of the inorganic fine particles are cited as below.

A-1 Colloidal silica partially modified by alumina (Aq. 30 wt. % solution, av. particle size of 14 nm)

A-2 Yttrium dioxide sol (Aq. 15 wt. % solution, av. particle size of 4 nm)

A-3 Antimony pentoxide sol (Aq. 30 wt. % solution, av. particle size of 50 nm)

A-4 Alumina sol (Aq. 30 wt. % solution, av. particle size of 14 nm)

A-5 Titanium dioxide sol (Aq. 10 wt. % solution, av. particle size of 14 nm)

A-6 Zinc oxide sol (Aq. 10 wt. % solution, av. particle size of 30 nm)

A-7 Zirconium oxide sol (Aq. 10 wt. % solution, av. particle size of 300 nm)

A-8 Tin dioxide sol (Aq. 30 wt. % solution, av. particle size of 14nm)

A-9 Vanadium pentoxide sol (Aq. 10 wt. % solution, av. particle size of 30 nm)

A-10 Colloidal silica partially modified by cerium (Aq. 30 wt. % solution, av. particle size of 20 nm)

A-11 Alumina sol partially modified by yttrium (Aq. 10 wt. % solution, av. particle size of 30 nm)

The oxide particles preferably be shelled with gelatin previously cross-linked so as to increase miscibility with gelatin.

The inorganic fine particles shelled with gelatin are the particles covered with a gelatin shell hardened with a cross-linking agent. Each of the particles may be covered with gelatin cross-linked or a plurality of the particles are gathered with each other in a form of alloy, which may be covered with the gelatin shell. The gelatin shell may have a thickness of 1 to 500 nm. The surface of the particles may be treated with a silane-coupling agent, aluminate com-

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pound or titanium compound to modify the miscibility thereof with gelatin, as disclosed JP-A 4-257849 and 6-95300 and then the shelling may be applied.

As the cross-linking agent, are cited hardening agents conventionally used for hardening gelatin. Among them, an aldehyde, triazine compound, vinylsulfon compound and carboxy-activating type hardener are preferably used.

The gelatin used includes an alkali-processed gelatin, acid-processed gelatin and phthalated gelatin. From the viewpoint of dispersion stability, the gelatin contains preferably calcium ions in an amount of 0 to 4000 ppm.

The particles cover with a gelatin shell are prepared in the following manner. After mixing a gelatin aqueous solution and an aqueous dispersion of inorganic fine particles, to the mixture was gradually added a cross-linking agent for gelatin with stirring with a high speed stirrer having sufficient shearing force such as a homomixer or impeller at a temperature of 30° to 80° C. Dispersing was allowed to continue for 1 to 72 hours at the temperature to obtain the gelatin-shelled particles. For the purpose of prohibiting coagulation during the dispersion, to the dispersing solution was added optimally a polyphosphoric salt such as sodium pyrophosphate, sodium hexametaphosphate or sodium triphosphosphate; polyhydric alcohol such as sorbitol, trimethylol-propane, trimethylol-ethane or trimethylol-methane; or nonionic polymer such as alkyl ester of polyethylene glycol.

Synthesis of the gelatin-shelled particles is exemplified as below.

#### 30 Synthesis Example-1 (MA-1)

Alkali-processed gelatin of 260 g was dissolved in water of 8750 ml. While being maintained at 40° C., was added thereto 1000 g of colloidal silica partially modified by alumina (30 wt. % aqueous solution; average size, 14 nm). To the resulting solution with stirring at a high speed with a homomixer was added 220 ml of 3.7% formalin solution over one minute and then stirring was allowed to continue further over a period of five hours. The resulting dispersion was filtered through a filter having a pore of 3 μm in diameter to remove coagulants.

#### 40 Synthesis Example-2 (MA-2)

A dispersion was prepared in the same manner as in the above described synthesis example-1, provided that to 1000 g of colloidal silica partially modified by alumina (30 wt. % aqueous solution; average size, 14 nm) to which was the same as in the example-1, was added 3.0 g of 3-glycidoxypentyl-trimethoxysilane with stirring at 50° C. for one hour was used and stirring was done at 50° C. for 10 hours.

#### 45 Synthesis Example-3 (MA-3)

A dispersion was prepared in the same manner as in the example-2, provided that the following titanium compound (TI) was used in place of silane coupling agent.

#### 50 Synthesis Example-4 (MA-4)

A dispersion was prepared in the same manner as in the example-1, provided that the following compound (RH) was used as a hardener.

#### 55 Synthesis Example-5 (MA-5)

A dispersion was prepared in the same manner as in the example-1, provided that acid-processed gelatin (TI) was used as a gelatin.

#### 60 Synthesis Example-6 (MA-6)

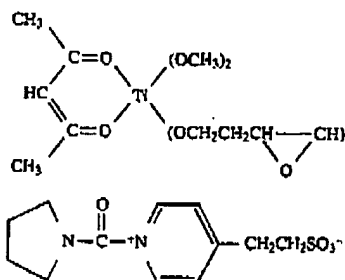
A dispersion was prepared in the same manner as in the example-1, provided that as inorganic particles was used antimony pentoxide (average size, 24 nm).

#### 65 Synthesis Example-7 (MA-7)

A dispersion was prepared in the same manner as in the example-2, provided that as inorganic particles was used antimony pentoxide (average size, 24 nm).

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Compound (TH)

Compound (RH)

The using amount of the inorganic fine particles of the invention is 0.05 to 1.0 g in dry weight ratio to gelatin used in a layer to be added, preferably, 0.1 to 0.7. The inorganic fine particles as above-described may be in combination.

Besides the organic aggregating particles of the invention, particles of polymethyl methacrylate, copolymer of methyl methacrylate and methacrylic acid, an organic compound such as starch or an inorganic compound such as silica, titanium dioxide, strontium sulfate or barium sulfate may be used simultaneously as a matting agent, as disclosed U.S. Pat. Nos. 2,992,101, 2,701,245, 4,142,894 and 4,396,706. The particle size thereof is 0.6 to 10  $\mu\text{m}$ , preferably, 1 to 5  $\mu\text{m}$ .

A silicone compound as disclosed in U.S. Pat. Nos. 3,489,576 and 4,047,958, colloidal silica as disclosed in Japanese Patent examined No. 56-23139, paraffin wax, higher fatty acid esters and starch derivatives may be incorporated, as a sliding agent, in the surface layer of the inventive photographic element.

A polyol such as trimethylolpropane, pentanediol, butanediol, ethylene glycol or glycerin may be incorporated, as a plasticizer, in a component layer of the inventive photographic element.

For the purpose of improvement in pressure resistance, polymer latex may be incorporated in a component layer of the inventive photographic element. Preferable examples of polymer include homopolymer of alkylacrylate, copolymer thereof with acrylic acid or styrene, styrene-butadiene copolymer, a polymer comprising a monomer having an active methylene group, water-solubilizing group or a group capable of being cross-linked with gelatin or copolymer thereof. More preferable is a copolymer of, as main component, alkyl acrylate or styrene with a monomer having water-solubilizing group or a group capable of being cross-linked with gelatin to improve in miscibility with gelatin as a binder. Examples of a monomer having water-solubilizing group include acrylic acid, methacrylic acid, 2-acrylamide-2-methylpropane sulfonic acid and styrene sulfonic acid. Examples of a monomer having a group capable of being cross-linked with gelatin include glycidyl acrylate, glycidyl methacrylate and N-methylolacrylamide.

In the case when the inventive photographic element is employed as a both-sided X-ray photographic material for medical use, it is preferable to provide a crossover-shielding layer for the purpose of improvement in image sharpness. In the crossover-shielding layer, may be contained a dye in the form of a solid particle dispersion to absorb crossover light. Such a dye, if having such a structure as being soluble at a pH of 9 or more (alkali-soluble) and insoluble at a pH of 7 or less, is not specifically limited. From the decoloring at the time of developing, is preferable a compound of formula (I) as disclosed in JP-A 6-308670.

Preferable developing agent for developing a photographic light sensitive material of the invention include dihydroxybenzenes such as hydroquinone as disclosed in

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JP-A 15641 and 4-16841, paraaminophenols such as p-aminophenol, N-methyl-p-aminophenol and 2,4-diaminophenol and 3-pyrazolidones such as 1-phenyl-3-pyrazolidones including 1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone and 5,5-dimethyl-1-phenyl-3-pyrazolidone. Preferably, these compounds be used in combination thereof.

The amount to be used of the above paraaminophenol or 3-aminopyrazolidone is preferably 0.004 mol/liter or more, more preferably 0.04 to 0.12 mol/liter.

The total amount of dihydroxybenzenes, paraaminophenols and 3-pyrazolidones is preferably 0.1 mol/liter or less.

As a preserving agent, may be incorporated a sulfite such as sodium sulfite or a reductone such as piperidinohexose reductone. The addition amount thereof is preferably 0.2 to 1 mol/liter, more preferably, 0.3 to 0.6 mol/liter. It is preferable to add a large amount of ascorbic acid so as to improve processing stability.

As a pH-adjusting agent, may be incorporated an alkali agent such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium phosphate or sodium phosphite.

As a pH-buffering agent, may be used borate as described in JP-A 61-28708, saccharose as described in JP-A 60-93439, acetoxime, 5-sulfosalicylic acid, phosphate and carbonate. These compounds are contained in such an amount as to maintain a pH of a developer within a range of 9.0 to 13, preferably, 10 to 12.5.

There may be incorporated a dissolving aid such as polyethylene glycols and an ester thereof, a sensitizer such as quaternary ammonium salt, a development-accelerating agent and a surface active agent.

As an antisliver-slugging agent, may be incorporated an antisliver-stain agent as disclosed in JP-A 56-106244, sulfide and disulfide as disclosed in JP-A 3-51844, cysteine derivatives as disclosed in JP-A 5-289255 and a triazine compound.

As an organic restrainer, are usable an azole type antifoggants including indazoles, imidazoles, benzimidazoles, triazoles, benzotriazoles, tetrazoles and thiazoles. As an inorganic restrainer, are included sodium bromide, potassium bromide and potassium iodide. In addition, are usable compounds as described in L. F. A. Mason, "Photographic processing Chemistry", Focal Press (1966), pages 226-229. U.S. Pat. Nos. 2,193,015 and 2,592,364 and JP-A 48-64933.

As a chelating agent used for masking a calcium ion contaminated in tap-water used in a processing solution, is cited an organic chelating agent having a chelating stability constant with iron of 8 or more, as disclosed in JP-A 1-193853. As an inorganic chelating agent are cited sodium hexametaphosphate, calcium hexametaphosphate and a polyphosphate salt.

As a developer hardener, are usable dialdehyde compounds. Among these compounds, is preferably used glutaraldehyde.

In the invention, replenishment, which corresponds to processing exhaustion and oxidative exhaustion is conducted at a rate of 35 to 98 ml per  $\text{m}^2$  of photographic element. A replenishing method may be the replenishment depending on the width of a photographic material and transporting speed thereof as disclosed in JP-A 55-126243; area-monitoring replenishment as disclosed in JP-A 60-104946 and area-monitoring replenishment controlled by the number of running-processed films as disclosed in JP-A 1-149256.

A preferable fixer may contain fixing materials conventionally used in the art. The pH of a fixer is 3.8 or more,

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preferably 4.2 to 5.5. Examples of fixing agents include thiosulfates such as ammonium thiosulfate and sodium thiosulfate and ammonium thiosulfate is preferable from the viewpoint of the fixing speed. A concentration of ammonium thiosulfate is preferably 0.1 to 5 mol/liter, more preferably 0.8 to 3 mol/liter.

In the invention, there may be used an acid hardening fixer, in which an aluminium ion is preferably used as a hardener. For example, it is preferable to add in the of aluminium sulfate, aluminium chloride and potassium alum.

In addition, the fixer may optionally contain a preserver such as a sulfite or bisulfite; pH-buffering agent such as acetic acid or boric acid; pH-adjusting agent including various acids such as mineral acid (sulfuric acid and nitric acid), organic acid (citric acid, oxalic acid and maleic acid) and chloric acid, and metal hydroxide (potassium hydroxide and sodium hydroxide); and chelating agent having capability of softening hard water.

As a fixing-accelerator is cited a thiourea derivative as disclosed in Japanese Patent examined 45-35754, 58-122535 and 58-122536 or a thioether as disclosed in U.S. Pat. No. 4,126,459.

It is preferable that a silver halide emulsion layer of the invention has a swelling-in-water ratio at processing of 150 to 250% and a swelled layer thickness is 70  $\mu$ m or less. When the swelling ratio exceeds 250%, drying defects occur, causing a tracking problem in automatic processor processing, particularly when rapid-processed. When the swelling ratio is less than 150%, developing unevenness and residual color are liable to be caused. The term, "swelling-in-water ratio" is defined as being a difference of layer thickness between after and before swelling, divided by a layer thickness before swelling and multiplied by 100.

The photographic element of the invention displays excellent performance in rapid processing within a total processing time of 10 to 30 seconds with an automatic processor. In the rapid processing of the invention, the temperature and time of processing steps such as developing and fixing are respectively 25° to 50° C. and 15 sec. or less for each step, and preferably 30° to 40° C. and 2 to 10 sec. In the invention, the photographic material is developed and fixed, followed by washing. In the invention, washing by counter current flow with 2 or 3 stages is conducted to save water. When washing with a small amount of water, it is preferable to install a washing bath provided with a squeegee roller. The washing temperature and time are preferably 5° to 50° C. and 2 to 10 sec., respectively.

The photographic material of the invention is developed, fixed, washed and then dried via a squeegee roller. The photographic material is dried by the way of heat-air convection drying, radiation drying with a far-infrared heater or heat-transfer drying with a heat-roller. The drying temperature and time are 40° to 100° C. and 4 to 15 sec., respectively. The total processing time in the invention refers to the time through which the photographic material is inserted to the inlet of a processor, and thereafter it passes through a developing bath, a cross-over section, a fixing bath, a cross-over section, washing bath, a cross-over section and a drying zone until the top of the photographic material reaches drying section outlet. In the silver halide photographic material of the invention, it is possible to reduce the amount of gelatin used as a binder in an emulsion layer and protective layer without deteriorating pressure resistance so that rapid processing can be completed within a total processing time of 10 to 30 sec.

#### EXAMPLES

Preferable embodiments of the present invention will be explained as below.

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#### Example 1

##### Preparation of a seed grain emulsion

A1	Oscin gelatin	24.2 g
	Water	9657 ml
	Sodium polypropyleneoxy-polyethyleneoxydisuccinate (10% ethanol solution)	6.78 ml
	Potassium bromide	10.8 g
	10% nitric acid	114 ml
B1	2.5N Silver nitrate aqueous solution	2825 ml
C1	Potassium bromide	824 g
	Potassium iodide	23.5 g
	Water to make	2825 ml
D1	1.75N Potassium bromide aqueous solution	
	An amount necessary for control silver potential	

To Solution A1 at 35° C. with stirring by a mixer as described in Japanese Patent examined Nos. 58-58288 and 58-58289, were added 464.3 ml each of Solutions B1 and C1 by a double jet method over a period of 1.5 min. to form nucleus grains. After interrupting the addition of Solutions B1 and C1, the temperature of Solution A1 was raised to 60° C. by taking 60 min. and the pH thereof was adjusted to 5.0 with 3% KOH solution. Thereafter, Solutions of B1 and C1 were added by a double jet method at a rate of 55.4 ml/min. over a period of 42 min. Silver potentials over the period of time of raising a temperature from 35° to 60° C. and of the double jet-addition of Solutions of B1 and C1 were controlled so as to be maintained at 8 and 16 mv, respectively, using Solution D1. The silver potential was measured using a silver ion-selecting electrode with a saturated silver-silver chloride electrode as a reference electrode.

After completing addition, the pH thereof was adjusted to 6 with 3% KOH solution and the emulsion was subjected to desalting-washing. It was proved by electron microscopic observation that the resulting seed grain emulsion was comprised hexagonal tabular grains having a maximum adjacent edge ratio of 1.0 to 2.0 and accounting for 90% or more of the projected area of total silver halide grains contained in the emulsion, the hexagonal tabular grains having an average thickness of 0.06  $\mu$ m and an average diameter (circle equivalent diameter) of 0.59  $\mu$ m. Coefficients of variation of the thickness and distance between twin planes were 40 and 42%, respectively.

##### Preparation of Emulsion Em-1

Using the above-described seed emulsion and the following four kinds of solutions, there was prepared an emulsion containing tabular grains having a core/shell structure.

A2	Oscin gelatin	11.7 g
	Sodium polypropyleneoxy-polyethyleneoxydisuccinate (10% ethanol solution)	1.4 ml
	Seed emulsion	0.1 mol equivalent
	Water to make	550 ml
B2	Oscin gelatin	5.9 g
	Potassium bromide	6.2 g
	Potassium iodide	0.8 g
	Water to make	145 ml
C2	Silver nitrate	10.1 g
	Water to make	145 ml
D2	Oscin gelatin	6.1 g
	Potassium bromide	94 g
	Water to make	304 ml
E2	Silver nitrate	137 g
	Water to make	304 ml

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To Solution A2 at 67° C. with vigorously stirring, were added Solutions of B2 and C2 by a double jet method over a period of 58 min. and then, Solutions of D2 and E2 were added by a double jet method over a period of 48 min., while maintained at a pH and pAg of 5.8 and 8.7, respectively.

After completing addition, the emulsion was subjected to desalination-washing. The resulting emulsion had respectively a pAg and pH of 8.5 and 5.85 at 40° C., containing 0.5 mol % iodide on the average.

It was proved by electron microscopic observation that 81% or more of the total projected area of silver halide grains accounted for by tabular grains having an average grain size of 0.96  $\mu$ m, a grain size distribution width of 19% and an average aspect ratio of 4.5. The average of distances between twin planes (a) was 0.019  $\mu$ m and coefficient of variation of (a) was 28%.

#### Preparation of Seed Grain Emulsion-2 Seed Emulsion -2 Was Prepared in the Following Manner.

A4	Oscin gelatin	100 g
	Potassium bromide	2.05 g
	Water to make	11.5 l
B4	Oscin gelatin	55 g
	Potassium bromide	65 g
	Potassium iodide	1.8 g
	0.2N Sulfuric acid	38.5 ml
	Water to make	2.6 l
C4	Oscin gelatin	75 g
	Potassium bromide	950 g
	Potassium iodide	27 g
	Water to make	3.0 l
D3	Silver nitrate	95 g
	Water to make	2.7 l
E2	Silver nitrate	1410 g
	Water to make	3.2 l

To a reaction vessel containing Solution A4 maintained at 60° C., were added Solutions B4 and C4 by a controlled double jet method over a period of 30 min. and then Solutions C4 and E2 were added by a controlled double jet method over a period of 105 min. The addition was carried out at a stirring of 500 rpm and at a flow rate that produced no new clear and did not cause Ostwald ripening to widen a grain-size distribution. The pAg at the time of adding silver ion and halide ion solution was adjusted to 8.3 $\pm$ 0.05 by use of a potassium bromide solution and the pH was adjusted to 2.0 $\pm$ 0.1 by sulfuric acid.

After completing addition, the emulsion was adjusted to a pH of 6.0 and subjected to washing to remove excessive salts according to the procedure as described in Japanese Patent examined 35-16086.

It was revealed by electron microscopic observation that the resulting seed emulsion was comprised of cube-shaped and slightly chipped tetradecahedral grains having an average grain size of 0.27  $\mu$ m and a grain size distribution width (coefficient of variation of grain size) of 17%.

#### Preparation of Emulsion Em-2

Using the above-described seed emulsion and the following seven kinds of solutions, was prepared a monodispersed core/shell type grain emulsion.

A5	Oscin gelatin	10 g
	Aqueous ammonia solution	28 ml
	Glacial acetic acid	3 ml
	Seed emulsion-2	0.119 mol

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-continued

		equivalent
B5	Water to make	600 ml
	Oscin gelatin	0.8 g
	Potassium bromide	5 g
	potassium iodide	3 g
C5	Water to make	110 ml
	Oscin gelatin	2.0 g
	Potassium bromide	90 g
D4	Water to make	240 ml
	Silver nitrate	9.9 g
	Aqueous ammonia solution (28%)	7.0 ml
E3	Water to make	110 ml
	Silver nitrate	130 g
	Aqueous ammonia solution (28%)	100 ml
F1	Water to make	210 ml
	Potassium bromide	94 g
G1	Water to make	163 ml
	Silver nitrate	9.9 g
	Aqueous ammonia solution (28%)	7.0 ml
	Water to make	110 ml

Solution A5 was maintained at 40° C. with stirring at 800 rpm with a stirrer. The solution was adjusted to a pH of 9.90 by acetic acid and was added thereto Seed emulsion-2 to form a suspension, and then Solution G1 was added at a constant rate over a period of 7 min. to make a pAg of 7.3. Further, Solutions B5 and D4 were simultaneously added over a period of 20 min. The pH and pAg thereof were adjusted to 8.83 and 9.0 over a period of 10 min. with potassium bromide aqueous solution and acetic acid; then, Solutions C5 and E3 were further added simultaneously over a period of 30 min.

The ratio of a flow rate at start to that at finish was 1:10 and the flow rate was increased with time. The pH was lowered from 8.83 to 8.00 in proportion to the flow rate ratio. When two thirds of Solutions C5 and E3 was added, Solution F1 was further added at a constant rate over a period of 8 min., wherein the pAg was increased from 9.0 to 11.0 and the pH was adjusted to 6.0.

Next, in a similar manner to emulsion Em-1, a monodispersed core/shell type grain emulsion was prepared, comprising slightly-rounded tetradecahedral grains having an average size of 0.40  $\mu$ m, an average iodide content of 2 mol %, grain size distribution width of 14% and an average aspect ratio of 1.2.

Thus prepared emulsions (Em-1 and Em-2) were heated to 60° C. and thereto was added a given amount of spectral sensitizing dyes as below, in the form of a solid particle dispersion. Thereafter, was further added a mixture solution of adenine, ammonium thiocyanate, chloroauric acid and sodium thiosulfate and triphenylphosphine selenide in the form of a solid particle dispersion. After 60 min., silver iodide fine grains were added and ripening was conducted over a period of 2 hr. in total.

When having completed the ripening, was added a given amount of 4-hydroxy-6-methyl-1,3,3a, 7-tetraazindene (TAI) as a stabilizer.

Spectral sensitizing dye (A)	120 mg
Spectral sensitizing dye (B)	2.0 mg
Adenine	15 mg
Potassium thiocyanate	95 mg
Chloroauric acid	2.5 mg
Sodium thiosulfate, amount as shown in Table 1	
Triphenylphosphine selenide, amount as shown in Table 1	
Silver iodide fine grains	280 mg
TAI	50 mg

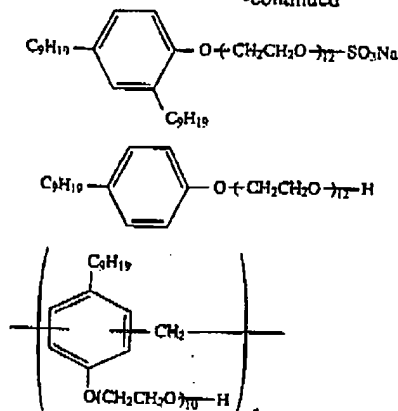
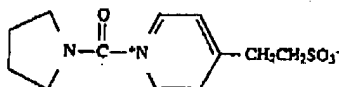
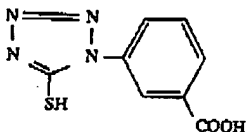
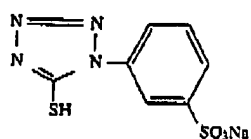
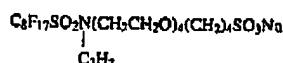
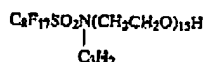
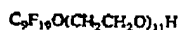
Solid particle dispersions of spectral sensitizing dyes and triphenylphosphine selenide were each prepared according



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-continued

(a mixture of  $n = 2-5$ )

## 1) Evaluation of Sensitivity

Samples, after aged at 23° C. and 55% R.H. for three days, were each sandwiched with intensifying screens for X-ray photography use, KO-250 (Product of Konica), exposed to X-ray through Penetrometer type B and processed with a developer and fixer having the following compositions under the conditions as below using a roller-transport type automatic processor SRX-501 (product of Konica). Swell ratio during processing of each sample was within a range of 180 to 220%.

Processing condition:

Step	Temp.	Time
Developing	35° C.	14.0 sec.
Fixing	34° C.	9.7 sec.
Washing	26° C.	9.0 sec.
Squeezing		2.4 sec.
Drying	55° C.	8.3 sec.
Total	(dry to dry)	43.4 sec.

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Composition of developer:

## Part A (to make 12 l)

5	Potassium hydroxide	450 g
	Potassium sulfite (50% solution)	2280 g
	Diethylenetriaminepentaacetate	120 g
	Sodium hydrogen carbonate	132 g
	5-Methylbenzotriazole	1.2 g
	1-Phenyl-5-mercaptotriazole	0.2 g
10	Hydroquinone	340 g
	Water to make	5000 ml

## Part-B (to make 12 l)

	Glacial acetic acid	170 g
	Trichylene glycol	185 g
15	1-Phenyl-3-pyrazolidone	22 g
	5-Nitroindazole	0.4 g
	Starter	
	Glacial acetic acid	120 g
	Potassium bromide	225 g
	Water to make	1.0 l

## Composition of Fixer:

## Part-A (to make 18 l)

	Ammonium thiosulfate (70 wt./vol. %)	6000 g
	Sodium sulfite	110 g
25	Sodium acetate trihydrate	450 g
	Sodium citrate	50 g
	Gluconic acid	70 g
	1-(N,N-dimethylamino)-ethyl-5-mercaptotriazole	18 g

## Part-B (to make 18 l)

30	Aluminum sulfate	800 g
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To prepare the developer, Parts A and B were simultaneously added to 5 liters of water and with stirring, was further added water to make 12 liters in total, followed by adjusting a pH thereof to 10.40 with acetic acid. The resulting solution was made a developer replenishing solution. To this replenishing solution was added the starter as above-described of 20 ml per 1 liter, followed by adjusting a pH to 10.26 to make a working solution.

To about 5 liter of water were added simultaneously Part A and B with stirring and water was further added to make 18 liter in total, followed by adjusting a pH thereof to 4.0 with sulfuric acid and sodium hydroxide. The resulting solution was used as a fixer replenishing solution.

Sensitivity was defined as a relative value of reciprocal of exposure amount required for giving a density of fog +1.0, in which the sensitivity of sample 1 was set to 100.

## 2) Evaluation of Roller Mark

The sample was exposed overall in such an amount that gives a density of 1.0, and processed in the manner as above-described. In the processing were used a development transport rack and crossover rack between a developer bath and fixer bath which were fatigued. Transport rollers of each rack had uneven surface having a peak to valley distance of about 10  $\mu$ m caused by fatigue.

After processed, occurrence of fine spot-like uneven density caused by pressure due to the uneven surface was observed particularly in a sample deteriorated in pressure resistance.

The level thereof was visually evaluated based on the following criteria.

5: No occurrence of spot

4: Slight occurrence of spots with no problem in practical use

3: Occurrence of a small number of spots at an allowable level of causing no occurrence of spots in normal rack.

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2: Occurrence of spots at a level of causing to occur spots even in a normal rack.

1: Occurrence of a large number of spots at a level of causing to occur spots always in a normal rack.

Results thereof are shown in Table 1.

TABLE 1

Sample No.	Emulsion	Gelatin content (g/m <sup>2</sup> )	Sensitizer		Inorganic fine particles	Organic aggregation particles	Sensitivity	Roller mark
			S	Se				
1 (C)	Em-1	2.7	2.8	0	None	Comp. n	100	3
2 (C)	Em-1	2.7	2.8	0	None	B-1	100	3
3 (C)	Em-1	2.3	2.8	0	None	Comp. a	120	2
4 (I)	Em-1	2.3	2.8	0	None	B-1	120	4
5 (I)	Em-1	1.8	2.8	0	None	B-1	140	4
6 (I)	Em-1	1.5	2.8	0	None	B-1	160	4
7 (I)	Em-1	1.8	2.8	0	None	B-11	140	4
8 (I)	Em-1	1.8	2.0	0.4	None	B-1	180	5
9 (I)	Em-1	1.8	2.8	0	A-1	B-1	150	5
10 (I)	Em-1	1.8	2.8	0	A-2	B-1	160	5
11 (I)	Em-1	1.8	2.8	0	A-3	B-1	160	5
12 (I)	Em-1	1.8	2.8	0	MA-1	B-1	155	5
13 (I)	Em-1	1.8	2.8	0	MA-2	B-1	160	5
14 (I)	Em-1	1.8	2.8	0	MA-7	B-1	160	5
15 (I)	Em-1	1.8	2.0	0.4	A-1	B-1	190	5
16 (I)	Em-1	1.8	2.0	0.4	A-2	B-1	200	5
17 (I)	Em-1	1.8	2.0	0.4	MA-1	B-1	195	5
18 (I)	Em-1	1.8	2.0	0.4	MA-2	B-1	200	5
19 (C)	Em-2	2.7	2.8	0	None	B-1	80	1
20 (I)	Em-2	2.3	2.8	0	None	B-1	100	4
21 (I)	Em-2	1.8	2.8	0	None	B-1	110	4
22 (I)	Em-2	1.5	2.8	0	None	B-1	120	4
23 (I)	Em-2	1.8	2.8	0	A-1	B-1	120	5
24 (I)	Em-2	1.8	2.8	0	A-2	B-1	130	5
25 (I)	Em-2	1.8	2.8	0	MA-1	B-1	125	5
26 (I)	Em-2	1.8	2.8	0	MA-2	B-1	130	5

C: Comparison

I: Invention

S: Sodium thiosulfate (mg/mol Ag)

Se: Triphenylphosphine selenide (mg/mol Ag)

Comp.a: Polymethyl methacrylate particles having an average size of 4.0  $\mu$ m

As can be seen from the table, it is proved that inventive samples were high in sensitivity and excellent in pressure resistance without occurrence of roller marks (spot).

#### Example 2

Samples Nos. 1 to 18 were exposed to X-ray and processed with the same developer and fixer as in Example 1 using a modified SRX-501 type processor at a higher transporting speed. Running processing was continued under the following processing condition 1 or 2 until a steady state was reached to prepare running-equilibrium solutions 1 and 2.

Ultra-Rapid Processing (B)

	Temp.	Time
Developing	38° C.	7.0 sec.
Fixing	37° C.	4.0 sec.
Washing	26° C.	7.0
Squeezing		2.4 sec.
Drying	58° C.	4.0 sec.
Total	(Dry to dry)	24.4 sec.

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Replenishing rates were varied as below:

	(Condition 1)	(Condition 2)
Developer-replenishing rate	14.0 ml* (180 ml/m <sup>2</sup> )	7.0 ml* (90 ml/m <sup>2</sup> )
Fixer-replenishing rate	14.0 ml* (180 ml/m <sup>2</sup> )	7.0 ml* (90 ml/m <sup>2</sup> )

(\*: per sheet having a size of 10 × 12 inches)

Samples Nos. 1 to 13 were processed with the above running equilibrium solution 1 (Condition 1) or 2 (condition 2) under the ultra-rapid processing condition B, and evaluated with respect to sensitivity and roller marks.

TABLE 2

Sample No.	Sensitivity		Roller mark	
	Condition 1	Condition 2	Condition 1	Condition 2
1	100	50	1	1
2	100	60	1	1
3	120	60	1	1
4	120	100	4	4
5	140	120	4	4
6	160	140	4	4
7	140	120	4	4
8	180	170	5	5
9	150	130	5	5
10	160	145	5	5
11	160	145	5	5
12	160	150	5	5
13	160	150	5	5
14	160	150	5	5

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TABLE 2-continued

Sample No.	Sensitivity		Roller mark	
	Condition 1	Condition 2	Condition 1	Condition 2
15	190	180	5	5
16	200	195	5	5
17	195	185	5	5
18	195	185	5	5

As can be seen from Table 2, inventive samples were shown to be little lowering in sensitivity and excellent in pressure resistance without occurrence of roller mark, as compared to comparative samples.

What is claimed is:

1. A silver halide photographic element comprising a support having, on at least one side thereof, a light-sensitive silver halide emulsion layer and a nonlight-sensitive hydrophilic colloidal layer, wherein said nonlight-sensitive layer contains organic material-aggregation particles; and gelatin contained in the total hydrophilic colloidal layers provided on one side of the support amounts to a range of 1.3 to 2.5 g per m<sup>2</sup> of a photographic element.

2. The photographic element of claim 1, wherein said aggregation particles have an average size of 1.0 to 20.0  $\mu$ m and are comprised of fine particles in an aggregated form; said fine particles having an average size of 0.05 to 0.50  $\mu$ m and comprising polyalkyl methacrylate, polyalkyl acrylate or polystyrene.

3. The photographic element of claim 2, wherein said aggregation particles are contained in an amount of 10 to 200 mg per m<sup>2</sup> of the photographic element.

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4. The photographic element of claim 1, wherein said silver halide emulsion layer contains tabular grains having an average aspect ratio of grain diameter to thickness of 2 or more and accounting for 50% or more of the total projected area of grains contained in the emulsion layer.

5. The photographic element of claim 4, wherein said tabular grains are selenium-sensitized.

6. The photographic element of claim 4, wherein said tabular grains comprise silver iodobromide or silver iodochlorobromide.

7. The photographic element of claim 1, wherein said silver halide emulsion layer further contains inorganic fine grains having an average grain size of 1 to 300 nm and comprising a silicon oxide, aluminium oxide, antimony oxide, titanium oxide, zinc oxide, niobium oxide, zirconium oxide, tin oxide, vanadium oxide or yttrium oxide.

8. The photographic element of claim 7, wherein said inorganic fine grains comprise silicon oxide, antimony oxide or yttrium oxide.

9. The silver halide photographic element of claim 7, wherein said inorganic fine grains are each covered with a gelatin shell.

10. A method of processing the photographic element as claimed in claim 1 with an automatic processor, comprising developing the exposed photographic element in a developer, fixing the element in a fixer, washing and drying, wherein said developer is replenished by a developer-replenishing solution at a rate of 35 to 94 ml/m<sup>2</sup> of the element, said photographic element being processed over a period of time of 10 to 30 seconds in total.

\* \* \* \* \*



**RELATED PROCEEDINGS APPENDIX**

The decision for Appeal No. 2006-0712 before the Board of Patent Appeals and Interferences is attached. This appeal involved a rejection over U.S. Patent 5,549,880 to Koksang.

4w 2950.32-05-03

The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

## UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCESEx parte XIANGXIN BI, NOBUYUKI KAMBE,  
SUJEET KUMAR, and  
JAMES T. GARDNERAppeal No. 2006-0712  
Application No. 09/606,884

ON BRIEF

MAILED

MAR 09 2006

U.S. PATENT AND TRADEMARK OFFICE  
BOARD OF PATENT APPEALS  
AND INTERFERENCESRECEIVED  
DOCKETING

MAR 13 2006

PATTERSON, THUENTE, SKAAR  
& CHRISTENSEN, P.A.

Before GARRIS, WARREN, and WALTZ, Administrative Patent Judges.  
WALTZ, Administrative Patent Judge.

## DECISION ON APPEAL

This is a decision on an appeal from the primary examiner's final rejection of claims 47 through 52.<sup>1</sup> The remaining claims pending in this application are claims 1, 4 through 11, 13 through 28, and 30 through 46, all of which have been allowed by the

<sup>1</sup>An amendment subsequent to the final rejection was submitted by appellants and entered by the examiner (see the amendment dated Mar. 5, 2004, entered as per the Advisory Action dated Mar. 23, 2004; Brief, page 2). We note that the word "collection" in claims 48-50 does not find antecedent basis in claim 47.

Appeal No. 2006-0712  
Application No. 09/606,884

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examiner (Brief, page 2; Answer, page 2, ¶(3)). We have jurisdiction pursuant to 35 U.S.C. § 134.

According to appellants, the invention is directed to cathode compositions comprising submicron vanadium oxide particles and a binder, where these particles provide superior battery performance, especially in lithium-based batteries (Brief, page 2). Representative independent claim 47 is reproduced below:

47. A cathode composition comprising vanadium oxide particles having an average diameter from about 5 nm to about 500 nm and a binder.

The examiner has relied on Koksbang, U.S. Patent No. 5,549,880, issued on Aug. 27, 1996, as the sole evidence of unpatentability (Answer, page 3). Claims 47-52 stand rejected under 35 U.S.C. § 102(a) and (e) as anticipated by Koksbang (*id.*). For reasons stated in the Brief, Reply Brief, and below, we reverse the rejection on appeal.

#### OPINION

The examiner finds that Koksbang discloses secondary lithium batteries comprising a "lithiated vanadium oxide cathode active material," a lithium metal anode, and a polymer electrolyte or solid electrolyte separator, where the vanadium oxide particles are

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"in the form of a fine powder having a surprisingly small particle size on the order of 0.1 to 5 microns" (Answer, page 3).

The initial burden of establishing unpatentability, on any ground, rests with the examiner. See *In re Oetiker*, 977 F.2d 1443, 1445, 24 USPQ2d 1443, 1444 (Fed. Cir. 1992). As correctly argued by appellants (Brief, pages 8-10; Reply Brief, pages 2-3), Koksbang does not disclose or suggest that the range of particle sizes taught is an average size or diameter as required by claim 47 on appeal and the examiner has not convincingly established that the disclosure of Koksbang should be interpreted or construed as an "average" size or diameter (Answer, page 4). The examiner has cited the different methods of preparation taught by Koksbang as evidence that it is "reasonable" to interpret the range taught by the reference as a range of average particle sizes, which thus overlap with the claimed range (*id.*). This evidence is not convincing for the following reasons. As correctly argued by appellants (Reply Brief, page 2), there is no disclosure or suggestion in Koksbang that the variation in reaction starting materials or parameters would alter the product properties, e.g., the particle sizes of the product (see col. 4, ll. 15-65). Furthermore, Koksbang specifically teaches the criticality of the "particle size" of the product, disclosing a range of particle

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sizes but never disclosing or suggesting an average of particle sizes or diameters (col. 2, ll. 59-61; col. 5, ll. 1-6; and col. 6, ll. 56-60). We note that the examiner has not submitted any substantive evidence that the term "particle size" was known in this art to mean an average particle size.

The examiner has found that the vanadium oxide particles disclosed by Koksbang are in the form of a fine powder with a particle size "on the order of 0.1 to 5 microns" (Answer, page 3). However, the examiner admits that Koksbang discloses "a lithiated vanadium oxide cathode active material" (Answer, page 3), and Koksbang only discloses particle sizes for the lithium vanadium oxide product (col. 2, ll. 59-61; col. 5, ll. 1-6; and col. 6, ll. 56-61). We find no disclosure in Koksbang of any particle size for the vanadium oxide per se (e.g., see col. 4, ll. 15-40). We have construed the term "vanadium oxide particles" as found in claim 47 on appeal with "the broadest reasonable meaning of the words in their ordinary usage as they would be understood by one of ordinary skill in the art," taking into account any enlightenment of the term in the specification. *In re Morris*, 127 F.3d 1048, 1054, 44 USPQ2d 1023, 1027 (Fed. Cir. 1997). Appellants' specification discloses vanadium oxide nanoparticles per se, as well as the production of only vanadium oxide (see Figures 5-12; specification,

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page 4, ll. 19-21; page 5, l. 18-page 6, l. 17; and page 14, l. 8 et seq.). Although the transitional term "comprising" opens claim 47 on appeal to other elements or components,<sup>2</sup> we determine that the claimed "vanadium oxide particles," as understood by one of ordinary skill in this art and consistent with the specification, does not encompass other materials such as intercalated lithium.<sup>3</sup>

For the foregoing reasons and those set forth in the Brief and Reply Brief, we determine that the examiner has failed to establish a prima facie case of anticipation in view of Koksang. Therefore we cannot sustain the rejection on appeal.

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<sup>2</sup>See *Vehicular Techs. v. Titan Wheel Int'l, Inc.*, 212 F.3d 1377, 1383, 54 USPQ2d 1841, 1845 (Fed. Cir. 2000) ("A drafter uses the term 'comprising' to mean 'I claim at least what follows and potentially more.'").

<sup>3</sup>See related Appl. No. 09/246,076, now U.S. Patent No. 6,225,007 B1, issued May 1, 2001.


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Application No. 09/606,884

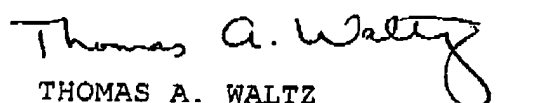
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The decision of the examiner is reversed.

**REVERSED**

  
BRADLEY R. GARRIS  
Administrative Patent Judge

  
CHARLES F. WARREN  
Administrative Patent Judge

  
THOMAS A. WALTZ  
Administrative Patent Judge

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TAW/sld

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